PB85-211985

Exposure and Risk Assessment for Copper

Little (Arthur D.), Inc., Cambridge, MA

Prepared for

Environmental Protection Agency, Washington, DC

Sep 80

U.S. Department of Commerce
National Technical Information Service
NTIS

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. EPA-440/4-81-015	2.	3. Recipient's Accession No. PB85 211985/AS

4. Title and Subtitle
An Exposure and Risk Assessment for Copper

5. Report Date
September 1980

6.

7. Author(s) Perwak, J.; Bysshe, S.; Goyer, M.; Nelken, L.; Scow, K.; Walker, P.; and Wallace, D.

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Arthur D. Little, Inc.
20 Acorn Park
Cambridge, MA 02140

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) 68-01-3857
(G)

12. Sponsoring Organization Name and Address
Monitoring and Data Support Division
Office of Water Regulations and Standards
U.S. Environmental Protection Agency
Washington, D.C. 20460

13. Type of Report & Period Covered
Final

14.

15. Supplementary Notes

Extensive Bibliographies

16. Abstract (Limit: 200 words)

This report assesses the risk of exposure to copper. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in September 1980.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of copper in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to copper for various subpopulations.

17. Document Analysis a. Descriptors

Exposure
Risk
Water Pollution
Air Pollution
Effluents
Waste Disposal
Food Contamination
Toxic Diseases
Copper

b. Identifiers/Open-Ended Terms

Pollutant Pathways
Risk Assessment

c. COSATI Field/Group 06F 06T

18. Availability Statement
Release to Public

19. Security Class (This Report)
Unclassified

20. Security Class (This Page)
Unclassified

21. No. of Pages
122

22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce

PB85-211985

United States
Environmental Protection
Agency

Office of Water
Regulations and Standards (WH-553)
Washington DC 20460

September 1980
EPA-440/4-81-015

Water

EPA

An Exposure and Risk Assessment for Copper

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

DISCLAIMER

This is a contractor's final report, which has been reviewed by the Monitoring and Data Support Division, U.S. EPA. The contents do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

EPA-440/4-81-015
September 1980

AN EXPOSURE AND RISK ASSESSMENT
FOR COPPER

by

Joanne Perwak
Sara Bysshe, Muriel Goyer, Leslie Nelken, Kate Scow,
Pamela Walker, and Douglas Wallace
Arthur D. Little, Inc.

and

Charles Delos
U.S. Environmental Protection Agency

EPA Contract 68-01-3857

Monitoring and Data Support Division (WH-553)
Office of Water Regulations and Standards
Washington, D.C. 20460

OFFICE OF WATER REGULATIONS AND STANDARDS
OFFICE OF WATER AND WASTE MANAGEMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

1a

FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

Michael W. Slimak, Chief
Exposure Assessment Section
Monitoring & Data Support Division (WH-553)
Office of Water Regulations and Standards

TABLE OF CONTENTS

Page

LIST OF FIGURES vii

LIST OF TABLES ix

ACKNOWLEDGMENTS x

I. EXECUTIVE SUMMARY 1

II. INTRODUCTION 9

III. MATERIALS BALANCE 11

A. Introduction and Methodology 11
B. Materials Balance 11
  1. Primary and Secondary Copper Production 11
  2. Production in Which Copper is a Byproduct/Contaminant 19
  3. Environmental Release of Copper During Consumptive Use 21
  4. Other Sources 24
  5. Copper Disposal 27
C. Summary 29
  References 30

IV. DISTRIBUTION OF COPPER IN THE ENVIRONMENT 33

A. Monitoring Data 33
  1. Copper in Water 33
  2. Copper in Aquatic Organisms 37
  3. Copper in Plants 37
  4. Copper in Soil 39
  5. Copper in Air 39
    a. Work Environment 39
    b. Non-Work Environment 39
B. Environmental Fate 39
  1. Overview 39
    a. Methodology 39
    b. Major Environmental Pathways 40
    c. Important Fate Processes 40
  2. Physicochemical Pathways 44
    a. General Fate Discussion 44
    b. Atmospheric Transport 51
    c. Solid Wastes 56

TABLE OF CONTENTS (continued)

Page

d. Aqueous Industrial Discharge 60
e. POTW 64
f. Copper Sulfate Use 68
3. Biological Pathways 71
C. Summary 76
1. Distribution 76
2. General Fate 77
3. Specific Pathways 77
a. Air 77
b. Solid Waste 78
c. Industrial Wastewater 78
d. POTW's 78
e. Copper Sulfate Use 78
4. Biological Pathways 78
References 79

V. EFFECTS OF AND EXPOSURE TO COPPER--AQUATIC ORGANISMS 87

A. Effects of Copper 87
1. Introduction 87
2. Freshwater Organisms 88
a. Chronic/Sublethal Toxicity 88
b. Acute Toxicity 92
3. Marine Organisms 92
4. Other Studies 95
5. Factors Affecting the Toxicity of Copper 95
6. Conclusions 100
B. Exposure of Biota to Copper 101
1. Introduction 101
2. Monitoring Data 102
3. Ingestion 103
4. Fish Kills 103
5. Conclusions 103
References 106

VI. EFFECTS OF AND EXPOSURE TO COPPER--HUMANS 111

A. Human Toxicity 111
1. Introduction 111
a. Copper Deficiency 111
2. Metabolism and Bioaccumulation 112
3. Animal Studies 113
a. Carcinogenicity 113
b. Mutagenesis 115

TABLE OF CONTENTS (continued)

Page

        c. Adverse Reproductive Effects 116
        d. Other Toxicological Effects 119
        e. Copper-Metal Interactions 119
    4. Human Studies 121
        a. Ingestion 121
        b. Inhalation 122
        c. Dermal Exposure 122
        d. Copper Intrauterine Devices (IUD's) 123
    5. Overview 123
B. Human Exposure 125
    1. Introduction 125
    2. Ingestion 125
        a. Food 125
        b. Drinking Water 126
    3. Inhalation 126
    4. Medical Exposure 128
    5. Conclusions 128
    References 129

VII. RISK CONSIDERATIONS 137

A. Biota 137
B. Humans 146
C. Conclusions 149
    References 150

APPENDIX FOUR CASE STUDIES--COPPER RISK TO AQUATIC ORGANISMS 153

LIST OF FIGURES

Figure No.		Page
1	Materials Balance of Copper	14
2	Typical Process Flowsheet for Copper Extraction and Refining	16
3	Locations of Major Copper Mines in the United States	17
4	Wood Processing Regions of the United States	22
5	Distribution of Total Copper in U.S. River Basins	34
6	Major Environmental Pathways of Copper Releases	42
7	Schematic Diagram of Major Pathways of Anthropogenic Copper Released to the Environment in the United States	44
8	Solubility Diagram of Cu(II) in Equilibrium with Malachite, Azurite, and Tenorite from pH 0-14	46
9	Adsorption of Heavy Metals in Oxidizing Fresh Waters (pH = 7, pE = 12, $pCO_2 = 10^{-3.5}$ atm. pCT - 4.16) As a Function of Surface Area of SiO_2	46
10	Adsorption of Heavy Metals on Soil Minerals and Oxides	51
11	Aerodynamic Particle Size Distribution of Copper in Industrial Stack Effluent	51
12	Monthly Deposition of Particulate Copper in New York City	55
13	The pH in Kerber Creek	59
14	Bicarbonate Concentrations in Kerber Creek	59
15	Dissolved Copper Concentration in Kerber Creek	59
16	Total Copper in Sewage at Grand Rapids, Michigan Before and After Pretreatment of Industrial Discharges to a POTW	67

LIST OF FIGURES (continued)

Figure No.		Page
17	Copper Concentration in Reservoir Sediment vs. Sediment Depth	71
18	Calculated Copper Speciation in a Relatively Hard Fresh Water Where Concentration of Inorganic Carbon = $10^{-2.3}$M and Calcium = $10^{-2.6}$M(a) in the Absence of Organic Chelation and (6) in Presence of Excess NTA ([NTA] total >>[Cu] total)	141

LIST OF TABLES

Table No.		Page
1	Summary of U.S. Copper Supply and Demand, 1976	12
2	Summary of Environmental Releases of Copper	13
3	Copper Releases from Mining and Milling Activities, 1978	18
4	Potential Environmental Release of Elemental Copper Related to Agriculture, 1976	20
5	Reported Copper Concentrations in POTW Influent	26
6	Summary of POTW Copper Budget	28
7	Total Copper in Ambient Waters by Region	35
8	Total Copper in Sediments in U.S. Regions, 1970-1979	36
9	Residues of Copper in Aquatic Organisms	38
10	Average Distribution of Copper in Three River Waters	46
11	Copper Concentrations as a Function of Water Hardness and Urbanization--Tributaries of Lake Cayuga, New York	47
12	Copper Concentration in Water and Sediments after Exposure to Zinc Outcrop	48
13	Bioconcentration Factors for Algae and Aquatic Invertebrates	72
14	Bioconcentration Ratios in Fish	74
15	Sublethal Effects of Copper on Freshwater Fish	89
16	Acute Toxicities of Copper for Freshwater Fishes	93
17	Chronic/Sublethal Effects of Copper on Marine Invertebrates	96
18	Reported Results from CEPEX Studies	97

LIST OF TABLES (continued)

Table No.		Page
19	Observed Copper Concentrations in U.S. Minor River Basins, 1978	104
20	Data for Copper-Related Fish Kills, 1971-1977	105
21	Effect of Copper Salts on Embryonic Development in the Hamster	118
22	Acute Toxicity of Copper Compounds	120
23	Outcome of Pregnancies with Copper IUD's Followed to Termination	124
24	Dietary Copper Intakes Reported in the Literature	127
25	River Basins with Factors Contributing to Risk For Aquatic Organisms	138
26	Distribution of Levels of Dissolved and Total Copper from STORET Monitoring Data	139
27	Adverse Effects of Copper on Mammals	147
28	Human Exposure to Copper	148

ACKNOWLEDGMENTS

The Arthur D. Little, Inc., task manager for this study was Joanne Perwak. Other major contributors were Muriel Goyer (human effects), Leslie Nelken (environmental fate), Gerald Schimke (materials balance), Kate Scow (biological fate), Pamela Walker (materials balance), Douglas Wallace (biota effects and exposure and monitoring data), Melba Wood (monitoring data), Sara Bysshe (aquatic effects and exposure), and Alfred Wechsler (technical review).

SECTION I.

EXECUTIVE SUMMARY

INTRODUCTION

The Monitoring and Data Support Division, Office of Water Planning and Standards, U.S. Environmental Protection Agency is conducting an ongoing program to identify the sources of and evaluate the exposure to the 129 priority pollutants. This report assesses the exposure to and risk associated with copper. The summary is organized somewhat differently than the report, focusing on the risk consideration first since this section presents the major conclusions of the study.

AQUATIC RISK CONSIDERATIONS

A consideration of the risk to aquatic organisms on the basis of laboratory bioassay data and ambient monitoring data implies risk in numerous locations in the United States. However, it is apparent that numerous factors influence the toxicity of copper in the field. The impact of these factors can only be evaluated on a case-by-case basis. Examination of four such locations indicated risk to aquatic organisms in three of them, although not as severe or widespread as would be predicted from laboratory data. In addition, this risk was not necessarily related solely to copper. Actual fish kills that have been reported in the past are commonly associated with mining areas and copper sulfate use and indicate a high potential for risk to aquatic organisms in these situations.

Toxicity: Toxicity data developed in the laboratory indicate that adverse effects are observed in salmonids at copper levels of 10 µg/L in soft water. Fathead minnow are affected at slightly higher concentrations. Numerous species experience lethal or sublethal effects at concentrations of 6 to 60 µg/L in the laboratory, generally in soft or moderately hard water. The fact that these levels (as total copper) are exceeded in numerous locations in the United States (55% of STORET observations), suggests that potential risk to fish and invertebrates is widespread.

Exposure: An analysis of monitoring data from STORET showed that mean concentrations were greater than 50 µg/L total copper in numerous minor river basins in 1978. These locations were primarily in the Southeast, the Ohio River Basin, the Lower Mississippi, and the Gila, Spokane, and Sacramento Rivers. In addition, some observations of greater than 120 µg/L were found in many of these locations. Further, examination of STORET data for individual stations in three of these minor river basins showed that elevated concentrations were generally limited to a few locations within each minor river basin. Thus, the mean of 50 µg/L is not representative of typical ambient conditions. In addition, soft waters generally were found in the Southeast, the Lower Mississippi, the Sabine and Neches Rivers, the Spokane River, and the Sacramento River, thus further increasing the potential risk in these areas.

Factors Influencing Risk: Numerous factors, however, complicate the direct comparison of monitoring data and laboratory toxicity data. First, only some chemical species of copper appear to be responsible for the observed effects. The cupric ion has been implicated and perhaps other soluble inorganic complexes as well. Copper in the form of organic complexes and adsorbed to particulates does not appear to be available to aquatic organisms.

The chemistry of copper can be very different in laboratory waters as compared with field situations. In the laboratory, concentrations of organic and suspended copper are generally low, making the relative presence of soluble inorganic species greater. In the field, free copper often comprises a very small portion of total measured copper (in some situations less than 1%) as compared with suspended and complexed copper. Thus, an overestimation of risk can result when monitoring data are assessed on the basis of laboratory toxicity data. Although locations with high copper concentrations have been identified, the extent to which these potentially toxic levels in specific areas are mitigated by complexation and adsorption is unknown.

Four areas with high reported copper levels were selected as case studies to examine specific sources of copper releases and the actual risk to aquatic biota in the vicinity: the Upper Sacramento River in California, the Coeur D'Alene River in Idaho, the Gila River in Arizona, and the Delaware River. Several conclusions can be drawn from this analysis:

- The use of major or minor river basin summaries from STORET, which are necessary when there are a large number of observations, can be misleading. In the examples cited, high concentrations are commonly limited to very localized conditions, usually one or two stations. In addition, a large amount of existing data is not yet included in the STORET system.

- Toxic effects as indicated by reduced populations of aquatic organisms have been observed in very localized areas during some periods. However, releases of copper appear to be rapidly diluted, precipitated, or adsorbed onto sediment. Despite occasionally high levels of copper, sensitive species have been observed during at least some parts of the year in these locations. Thus seasonal variations in pH, flow, etc., appear to affect greatly the level of exposure and, therefore, the risk to aquatic organisms.

- The sources of copper in the Gila, the Coeur D'Alene, and the Sacramento River Basins appear to be primarily mining activities, especially abandoned sites. The low pH of the surface waters in these areas makes the high copper levels even more significant since the cupric ion would be more prevalent.

- Levels of copper in the Delaware may well be lower than evidenced by STORET due to detection limits of some of the analyses. Further, the importance of copper as a contaminant of concern, in most areas, appears to far less than that of other contaminants in that drainage basin.

- In all cases, copper was not the only contaminant of concern. Zinc, cadmium, and/or iron were also considered to be problems in the mining areas. A large number of organic and inorganic contaminants exist in the Delaware River.

The case studies confirmed that aquatic organisms are at risk, at least in the Coeur D'Alene, Sacramento, and Gila Rivers. This risk, however, cannot be entirely ascribed to the effects of copper. The risk due to copper in the Delaware River could not be established.

HUMAN RISK CONSIDERATIONS

Copper does not appear to represent a significant risk to humans. It has not been shown to be carcinogenic, mutagenic, or teratogenic, even when its use in IUD's is considered. Thus the effects expected due to copper are primarily related to acute exposures, with the lowest oral lethal dose being 50 mg/kg. Since the maximum ingestion exposure is estimated to be 0.3 mg/kg/day (24 mg/day for a 70-kg person), a considerable margin of safety appears to exist. The only exposure route with a potential for toxic effects is renal dialysis. However, no problems with this type of exposure have been reported in the last few years.

Toxicity: Copper is an essential trace element in human and animal nutrition, and the total body content of the average adult ranges from 100 mg to 150 mg. Copper deficiency is a recognized problem and its symptoms are well known.

The net absorption efficiency of ingested copper is about 5%. Absorption through the skin is minimal. Absorption through the lungs is gradual and depends upon the solubility of the specific salt involved. Homeostatic mechanisms regulate copper levels in the human body quite effectively.

No experimental evidence exists to suggest that copper is tumorgenic in man or experimental animals. In fact, administration of copper may inhibit chemically induced tumors in laboratory animal. The use of copper IUD's has been investigated for dysplastic lesions of the cervix or precancerous lesions. Although dysplasia cases have been reported, no progression to cancer has been found, although further study is underway.

No clear evidence of mutagenicity exists, although enhanced transformation of hamster embryo cells by a simian adenovirus has been observed, and increased lethal mutations noted in Drosophila, but only at high concentrations. The results of bacterial assays have been negative or show mutagenic activity only at concentrations that are toxic to the bacterium. Further work is needed to clarify the mutagenic potential of copper.

Copper IUD's have been investigated for evidence of adverse reproductive effects. There are no data to suggest that intrauterine copper has teratogenic effects on the fetus, although an increase in spontaneous abortion has been observed in involuntary pregnancies with a copper IUD _in utero_ in a relatively small sample.

As far as other toxicological effects are concerned, there is a wide margin of safety between copper deficiency and copper toxicosis in mammalian species. The lowest reported lethal oral dose for humans is 50 mg/kg (copper sulfate). Survival after consumption of as much as 3 g copper sulfate has been reported. Acute copper poisoning produces tachycardia, hypotension, hemolytic anemia, oliguria, uremia, coma, cardiovascular collapse and death.

Exposure: Although further investigation is needed in some areas (i.e., the possibility of mutagenicity, and the potential for cervical cancer related to the use of copper IUD's), it appears that copper has a low order of toxicity to humans. Thus, worst case situations have been considered for copper exposure. The maximum reported intake of copper in food is 7.6 mg/day from diets containing liver, which is high in copper. The maximum likely intake from drinking water is 16.7 mg/day, primarily resulting from the use of copper in the water distribution system. Thus a total maximum exposure via ingestion would be approximately 24 mg/day. However, only an extremely small subpopulation would be exposed to this level; a more typical exposure through ingestion would be 1 to 4 mg/day. Since absorption via ingestion is about 5%, the actual absorbed dose would be considerably lower.

Inhalation exposures, even in worst case situations (for example, near smelters) are considerably lower than ingestion exposures, on the order of 0.04 mg/day.

Certain medical procedures may result in human exosure to copper. For example, copper sulfate used in the treatment of burned skin has been reported to result in symptoms of copper toxicosis though this type of incident appears to be rare.

Persons receiving kidney dialysis have also been exposed to high levels of copper, primarily due to source water or to equipment problems. Exposures of 5 mg have been reported, and the potential for a 240-mg exposure per dialysis has been calculated. Incidents of such exposures have not been reported recently, and it is probable that dialysis equipment has been improved in order to reduce exposure.

A large subpopulation of human females is exposed to copper through the use of copper IUD's. Such devices can release up to 50 ug copper/day, about one-half of which amount is lost in menstrual blood. The resultant exposure of 0.025 mg/day is available for absorption, whereas only 5% of ingested copper is absorbed.

SOURCES OF COPPER RELEASES TO THE ENVIRONMENT

In 1976, the total U.S. industrial demand for copper was 2.4 million metric tons (MT). Approximately 54% of this supply resulted from domestic mine production, 17% from industry stocks, 15% from scrap recylcing, and 14% from imports. This supply went largely into the production of copper wire and other electrical components (56%), with 24% being used for brass production. Thus these two industries accounted for the consumption of 80% of the industrial supply.

Of the total identified releases of copper to the environment, 97% went to land, 2.4% went to water, 0.3% went to POTW's, and 0.04% went to air. It should be pointed out that the uncertainties in this type of analysis are great, and the distribution of specific releases to specific environmental compartments is often based on very limited information. In addition, the transfer between compartments may be rapid. However, it is clear that the land receives by far the largest portion of copper release.

The major contributors of copper to land (97%) are the mines and mills in the form of tailings, overburden, etc. Disposal occurs primarily in the states of Arizona, Nevada, New Mexico, Utah, Tennessee, Michigan, and Montana.

Agricultural applications contribute about 2% of the pollutant loading to land, primarily in the Southeast, Pacific, Cornbelt and Appalachian regions. Other sources of copper to land include POTW's, municipal refuse, electroplaters, and iron and steel producers. There are numerous unquantified releases to land. These losses are primarily from copper-containing products during use, such as plumbing, gutters, roofing, radiators, etc.

Of the identified releases of copper to water (28,848 MT for 1976), the transport of eroded copper-containing soils is the most significant, representing about 68% of the total. This source, however, is widely distributed throughout the United States. Copper sulfate use represents about 13% of the identified releases to water, while urban runoff represents about 2%. Sources to urban runoff include exposed construction elements and transportation and industrial applications (plumbing, chrome, brass, etc.).

In addition, POTW's contribute about 8% of the total releases to water. While this represents a contribution by point sources, there are numerous locations where the releases occur. Sources of copper to POTW's include domestic wastes, which account for about 25% of the total copper entering water from POTW's; estimated known industrial releases account for an additional 20%. The remainder can probably be attributed to contributions from additional industrial and natural sources.

The remaining 9% of the direct releases to water is comprised of releases from electroplating (400 MT), abandoned mines (314 MT), iron or steel (656 MT) and various other industrial processes. Copper wire and brass production, although utilizing about 80% of the copper supply, release relatively low amounts to the aquatic environment, 134 and 151 MT, respectively.

Known releases of copper to the atmosphere (484 MT) include primarily emissions from smelting (41%), copper wire production (34%), and incineration of refuse (21%). Smaller amounts are released from brass production and iron and steel production.

The largest areas of uncertainties in this analysis are the estimated loadings of copper associated with suspended sediment, from abandoned metal mines, in urban runoff, and to POTW's. The releases from mining and other industrial operations are better defined. In addition, releases during the use of copper-containing products could be substantial, but these have not been specifically estimated. However, the reported contribution of copper in urban runoff may already contain some copper from these sources.

FATE AND DISTRIBUTION OF COPPER IN THE ENVIRONMENT

Monitoring Data: Copper is widely distributed in the environment since it is naturally occurring. Levels of total copper in the aquatic environment generally range from 1 μg/L to 100 μg/L, although higher concentrations are found near sources and more generally in New England, the Western Gulf, and the Lower Colorado River. Sediments generally contain levels between 1 mg/kg and 1000 mg/kg copper. Levels of copper in fish tissues are generally in the range of 1 mg/kg to 100 mg/kg. Molluscs, especially oysters, have accumulated levels as high as 1000 mg/kg. Copper is an essential micronutrient for plants and is found at levels of 1 mg/kg to 150 mg/kg. Copper deficiency is a common problem in crops.

Levels of copper in air range from 0.01 $\mu g/m^3$ to 0.3 $\mu g/m^3$, although levels near smelters can be 1 $\mu g/m^3$ to 2 $\mu g/m^3$.

Fate and Pathways Analysis: Since the largest portion of copper reaches the soil, it is important to consider the fate of copper in this compartment. In general, the behavior of copper in soils is dependent upon the adsorptive properties of the soil, as well as the pH and redox potential of the soil solution. At a pH of 5 or 6, adsorption is the principal means of limiting copper mobility. Above this pH, chemical precipitation becomes the more dominant fate process.

Specifically, the greatest portion of copper releases to land originate from solid waste and tailings from copper mining and milling. Currently, tailings are left to settle in lagoons following treatment with lime to raise the pH and precipitate heavy metals. Controlled conditions for these sites reduce the mobility of copper. However, former disposal sites are more subject to leaching and runoff and the resulting acid mine drainage affects both groundwaters and surface waters. The immediate effect on receiving waters is a drop in pH and bicarbonate concentration, as well as an increase in the concentration of copper and other metals. Stream recovery is a function of the distance downstream from the source as the copper concentration is rapidly reduced due to precipitation, adsorption and dilution.

A large, but not well quantified amount of copper is disposed of in municipal landfills. Although copper is the "least generally mobile" of the metals and is strongly adsorbed onto soil, it has been found in landfill leachate at levels of 0.1 mg/L to 1.0 mg/L.

The direct releases of copper to water are small relative to those going to land; however, resulting exposure may be important. In general, copper reaching the aquatic environment will be rapidly adsorbed on to suspended solids or bottom sediment. The form of the dissolved copper is highly dependent on the receiving water. Below a pH of about 7, the free ion will be important, whereas above this, the carbonate and hydroxy complexes will predominate. If organic complexing agents are present in sufficient amounts, organic complexes of copper will predominate over the entire pH range. Copper in the sediment may be associated with iron and manganese oxides, organic matter, clays and perhaps sulfides. It does not appear to be readily exchangeable or soluble in natural, alkaline waters.

Copper reaching the aquatic environment as a result of runoff is probably already adsorbed onto soil particles. The fate of this copper depends upon the fate of the suspended material.

Copper is also discharged as a constituent of wastewater effluents from electroplating, brass manufacture, etc. The concentration of copper in aqueous industrial discharges can be lowered by pretreatment. Once released, the copper is rapidly adsorbed and, in some cases, precipitated.

Copper is directly applied to the aquatic environment through its use as an algicide ($CuSO_4$). When added at levels of 0.4 g Cu^{2+} per m^2, levels in water are returned to baseline values within 24 hours. Copper is strongly adsorbed onto the sediment where it accumulates.

A small portion of copper releases reach the atmosphere. The forms of copper released due to thermal processes are the oxide, elemental copper as the vapor, and copper adsorbed to particulates; copper sulfide as the dust is the result of entrainment from coal pits.

Once copper has been released into the atmosphere, its residence time and distance traveled are dependent upon particle size, as well as meteorological factors. Copper from combustion sources (smelting, coal combustion, incineration) tends to be associated with sub-micron particulate matter. Such copper can be deposited via rainout or dry fallout. The residence time in the troposphere has been estimated as 7 to 30 days. Thus, while most deposition will occur in the vicinity of the source, some particulates may be carried considerable distances.

Copper deposited on pavements can contribute to urban runoff and represent a significant source to surface waters. Copper deposited on soils or surface waters is subject to the same factors, which affect direct releases to those compartments, primarily adsorption.

Copper entering POTW's is largely concentrated in the sludge, with about 25% to 75% being removed by treatment. The efficiency is dependent upon treatment method and influent concentration, with less removal occurring at higher concentrations in influent. Industrial pretreatment can reduce the concentration in the effluent and in the sludge from POTW's. Copper in effluents is subject to the factors affecting other releases to the water compartment; it appears to be rapidly diluted and adsorbed.

Sludge may go to a sanitary landfill or be spread for the purpose of amending soil. Although the form of copper in the sludge is not known, it does not appear to be readily translocated when applied to soil. Concentrations in leachate from sludge amended soils were less than 12 µg/L.

Copper reaching both the water and soil compartments can be taken up by biota. In aquatic environments, uptake depends on such factors as pH and water hardness. Molluscs, especially oysters, appear able to concentrate copper up to 30,000 times water concentrations. Field studies have shown that fish accumulate copper at concentrations one to two orders of magnitude over water concentrations. Uptake of copper from soil can also occur, although terrestrial plants are commonly deficient in this nutrient. However, concentrations of copper are increased in some plants cultivated on soil amended with sewage sludge.

SECTION II.

INTRODUCTION

The Office of Water Planning and Standards, Monitoring and Data Support Division of the Environmental Protection Agency is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated included potential harm to human beings and deleterious effects on fish and other biota. The goal of the task under which this report has been prepared is to integrate information on cultural and environmental flows of specific priority pollutants and estimate the risk based on receptor exposure to these substances. The results are intended to serve as a basis for developing suitable regulatory strategy for reducing the risk, if such action is indicated.

This report is intended to provide a brief, but comprehensive, summary of the production, use, distribution, fate, effects, exposure, and potential risks of copper. There are a number of problems with attempting such an analysis for this metal. Since the purpose of this report is to provide a basis for regulation, it is important to identify sources. However, copper is an element commonly found in the earth's crust and natural sources to waterways can be significant. Thus in any analysis of discharges or runoff, it is important to distinguish background concentrations or natural sources from anthropogenic sources. We have attempted to do this to the extent possible, but in discharges from Publicly Owned Treatment Works (POTW) facilities, for example, it is difficult to trace back to the sources, natural or anthropogenic.

In addition, the aquatic chemistry of copper is complex. Other metals are commonly found with copper, making this situation more complicated due to possible interactions. We have used information available on the aquatic chemistry of copper to draw conclusions regarding specific fate pathways as related to sources.

Finally, copper is a nutritional requirement, and copper deficiency could be considered a risk. However, for the purposes of this risk assessment we have discussed copper deficiency cursorily to establish a range of acceptable doses. We have concentrated on assessing the risks due to exposure to high levels of copper.

This report is organized as follows:

- Section III contains information on the production, discharge (point and non-point) and disposal of copper.

- Section IV describes available monitoring data and a consideration of the fate of copper in five specific pathways.

- Section V considers effects and exposure of biota to copper.
- Section VI discusses effects of copper on humans and describes exposure scenarios.
- Section VII discusses risk consideration for various subpopulations of humans and aquatic organisms, as a result of estimated exposure to copper.

SECTION III.

MATERIALS BALANCE

A. INTRODUCTION AND METHODOLOGY

In this section, a materials balance is developed for copper. The materials balance considers copper as it flows from the cultural environment to its first point of entry into the natural environment. Potential sources of copper releases were identified by a review of activities in which the material participates from its extraction and refining through processing, use, and disposal. Thus the materials balance encompasses all sources of pollutant release from the point at which copper enters the cultural environment until it has returned to the natural environment.

For each source of pollutant release, the amount of material released was estimated, and the environmental compartments (air, land, and water) initially receiving and transporting the element were identified, as were the locations at which the pollutant loadings take place. There are many uncertainties inherent in this type of analysis: not all current releases have been identified, past releases are not well documented, and future releases are difficult to predict. Nevertheless, sufficient information is available to indicate in general terms the nature, magnitude, locations, and time dependence of pollutant loading of the environment with copper.

B. MATERIALS BALANCE

In 1976, total U.S. industrial demand was 2.4 million metric tons (MT). Primary production of copper is expected to grow at an annual rate of 3% and secondary production at a rate of 5%. Table 1 summarizes the commercial sources and uses of copper.

Environmental releases during production and occurring due to various consumptive uses are presented in Table 2 and Figure 1. Copper is consumed primarily as the metal or alloys by industry. A remaining 0.5% is used forming copper compounds, largely copper sulfate (Versar, 1978). Of the industrially consumed metal, the majority is used by electrical and electronic equipment manufacturers; the construction, machinery and transportation industries are major consumers as well. Significant discharges to the environment occur during production and beneficiation processes. Discharges to water from Publicly Owned Treatment Works (POTW's) are also substantial.

1. Primary and Secondary Copper Production

Copper is mined and milled in seven states within the continental United States, and this provides a significant source of releases to the

TABLE 1. SUMMARY OF U.S. COPPER SUPPLY AND DEMAND, 1976

Source/Consumer	Supply (MT)	Consumption (MT)
Domestic mine production and beneficiation	1,287,940	
Refined Scrap	204,080	
Unrefined Scrap	149,660	
Imports (refined)	235,810	
Imports (ores-concentrates)	99,770	
Industry Stocks, 1 January 1976	419,940	
Copper Wire Mills		1,349,288
Brass Production		567,092
Other		39,110
Industry Stocks, 31 December 1976		441,710
Total	2,397,200	2,397,200

Note: The above figures are for one year (1976). There is considerable statistical variation from year to year; consequently, these do not not reflect average values.

Source: Versar, 1978.

TABLE 2. SUMMARY OF ENVIRONMENTAL RELEASES OF COPPER (Estimated 1976)

Source	Release (MT/yr) Air	Direct Aquatic	POTW	Land
Primary Production	Δ	13.4[2]	-	1,078,290[2]
Smelting	200[2]	Unknown		Unknown
Secondary Production	Δ	0.3[3]	7[3]	Δ
Metallic Ore Mining & Related Activities	Δ	34[3]	-	Unknown
Copper Wire Mills	164[1,2]	134[1]	1,484[1]	Δ
Brass Production	3[1,2]	151[1]	294[1]	42[1,2]
Iron & Steel Production	17[1,2]	656[3]	-	896[1,2]
Coal Mining**	Δ	181[1,2]	-	-
Pulp, Paper & Paperboard	-	110[3]	-	-
Inorganic Chemicals	-	4[3]	-	-
Steam Electric Industry	-	174[3]	-	-
Machinery Mfgr.	Δ	151[1]	-	-
Electroplating		400[3]	1,400[3]	920[3]
Miscellaneous Sources	-	72[3]	-	-
Area Sources:				
Abandoned Metal Mines	-	314[9]	-	-
Agricultural Applications	*	3,600[5]	*	19,195[4,5,6]
Urban Runoff	-	441[2]	84[2]	*
Suspended Sediment	-	18,400[2]	-	-
Incineration/Refuse	100[2]	-	-	1,900[2]
POTW	-	2,073[9]	-	9,680[8]
Total	484	26,909	3,269‡	1,110,923

ΔInsignificant

*These emissions are directly applied to the category in which they are reported; however, often during or shortly following release, they enter other environmental media.

**Coal combustion is known to release some copper; insufficient data is available to substantiate this quantity.

‡The total estimated POTW influent is 11,800 MT/yr (see Table 6). Thus, only a portion of the sources have been identified.

[1]Versar, 1978.

[1] Versar, 1978.

[2] Arthur D. Little Estimate.

[3] Effluent Guidelines Monitoring Data, analyzed by Versar, EPA, 1979.

[4] U.S. Department of Agriculture, 1974.

[5] SRI, 1979.

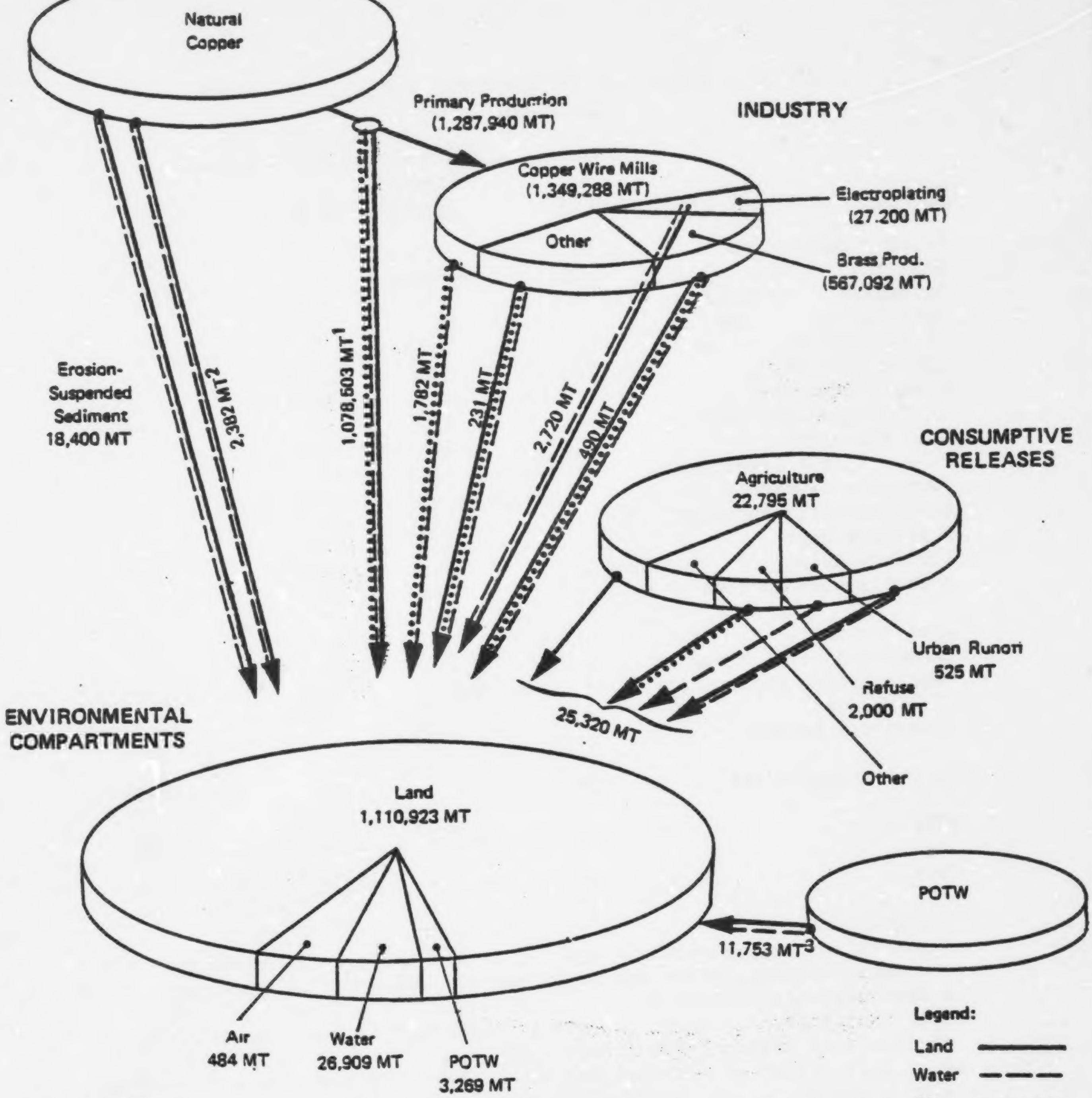
[6] EPA, 1974.

[7] EPA, 1977.

[8] Table 6.

[9] Martin and Mills (1976).

Reproduced from best available copy.


Natural Copper
Primary Production (1,287,940 MT)
INDUSTRY
Copper Wire Mills (1,349,288 MT)
Electroplating (27.200 MT)
Other
Brass Prod. (567,092 MT)
Erosion-Suspended Sediment 18,400 MT
2,382 MT2
1,078,503 MT1
1,782 MT
231 MT
2,720 MT
490 MT
CONSUMPTIVE RELEASES
Agriculture 22,795 MT
Urban Runoff 525 MT
Refuse 2,000 MT
Other
25,320 MT
ENVIRONMENTAL COMPARTMENTS
Land 1,110,923 MT
POTW
11,753 MT3
Air 484 MT
Water 26,909 MT
POTW 3,269 MT
Legend:
Land
Water
Air

( ) Copper Use

[1] Includes smelting

[2] Industrial releases in which copper exists as a trace element. Sources include iron and steel production, coal mining, pulp and paperboard manufacture, steam electricity generation, other ore mining, and abandoned mines.

[3] POTW effluent includes contributions from human and other unknown sources.

Note: Boundaries between receiving medium are often undefined and/or changing: Copper apparently released to one compartment can result in another.

Source: Arthur D. Little, Inc., based on 1976 estimates.

FIGURE 1. MATERIALS BALANCE OF COPPER

environment, particularly to land. A typical flowsheet for the copper production process is presented in Figure 2.

The general practice for sulfide ores (from which 88% of the copper is produced) is to mine the ore, then concentrate it in a milling plant to produce a concentrate for smelting and refining. Nine companies operate 17 smelters and 19 companies operate 23 refineries and electrowinning plants (Arthur D. Little, Inc., estimates, 1979). The other major process is the acid leaching of oxide ore and recovery from solution by cementation or electrolysis. Figure 3 shows the location of major copper mines.

Following extraction, the ore is crushed and concentrated by a flotation process involving organic reagents and water (milling). For a grade of ore of between 0.6% and 0.8% copper, the resulting concentrate is from 15% to 35% copper (NIOSH, 1975). The copper is then roasted in a reverbatory furnace and formed into a matte for smelting.

The major releases to land and water from mining and milling are presented by state in Table 3. The copper content in tailings represents that portion of the mineral that could not be recovered. Most of it is in the form of silicates and sulfides, which are relatively insoluble. Tailing ponds are contained by control structures that permit only rare opportunities for discharge. Large quantities of mine tailings that have accumulated from past mining practices constitute a source of copper as shown in Table 2.

Waterborne discharges of copper from active copper mines result from the concentrating process, the grinding process at the mill, and the thickening and settlement processes. For copper mining and milling operations situated in the West and Southwest, water is a scarce commodity, which is most often recycled rather than discharged. Of the 21 copper mining and milling operations in Arizona, only two discharge effluent. None of the operations in Nevada and New Mexico discharge any water at all (Arthur D. Little, Inc., estimates, 1979). Thus, in total, water discharges of copper from these processes are small.

Airborne releases of copper from the mining and milling processes are also insignificant. Economic as well as environmental factors provide incentives for maintaining an efficient recovery mechanism (e.g., bag houses). The relatively high price of copper on the current market makes it economically attractive to capture copper otherwise released to the atmosphere. The same situation exists in smeltering and other copper refining processes.

Seventeen primary copper smelters in the United States are operated by nine companies. All but two (in Tennessee and Michigan) are located in the western states of Arizona, Texas, Nevada, New Mexico, Montana and

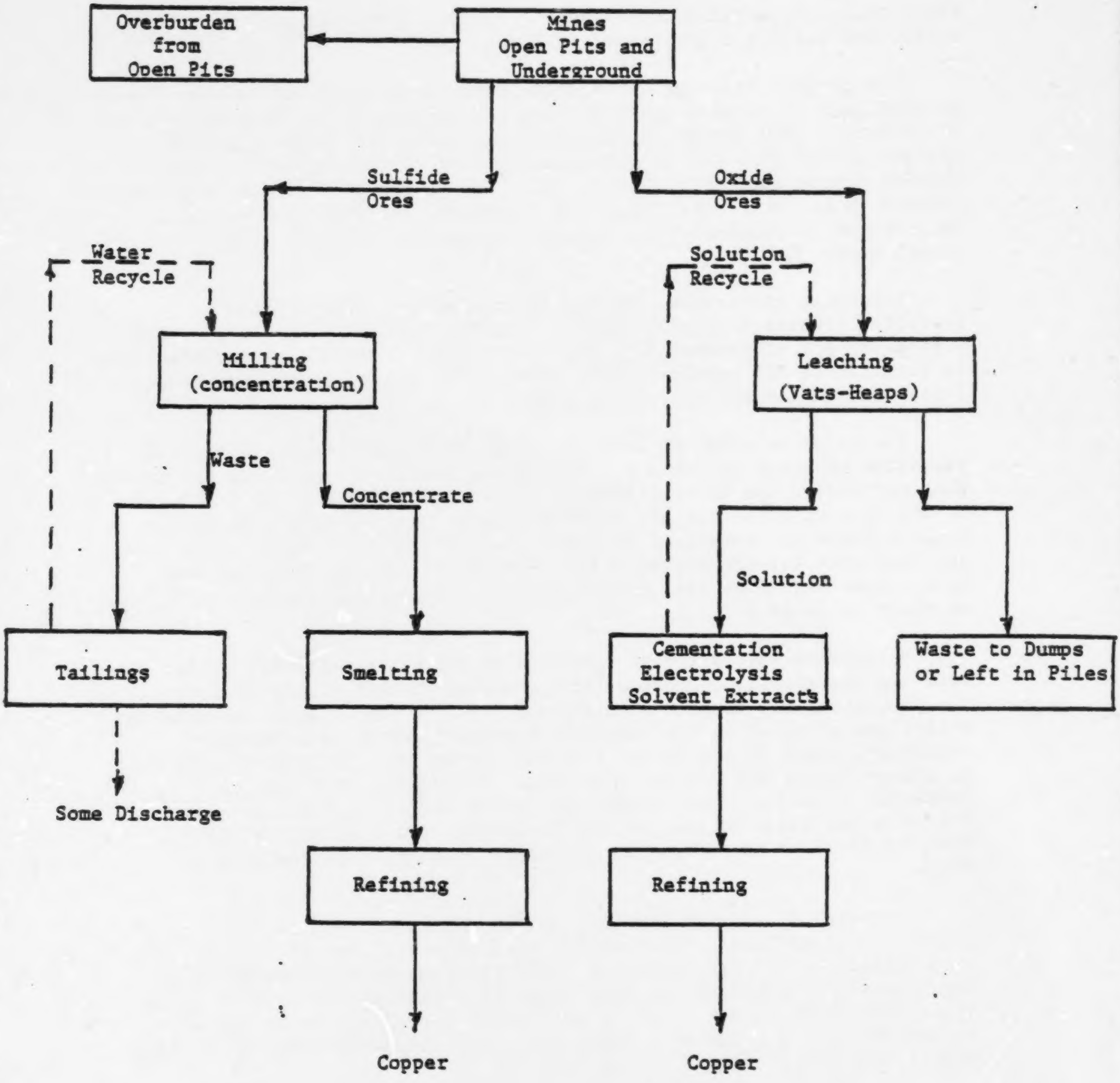

Overburden from Open Pits
Mines Open Pits and Underground
Sulfide Ores
Oxide Ores
Water Recycle
Solution Recycle
Milling (concentration)
Leaching (Vats-Heaps)
Waste
Concentrate
Solution
Tailings
Smelting
Cementation Electrolysis Solvent Extracts
Waste to Dumps or Left in Piles
Some Discharge
Refining
Refining
Copper
Copper

FIGURE 2. TYPICAL PROCESS FLOWSHEET FOR COPPER EXTRACTION AND REFINING

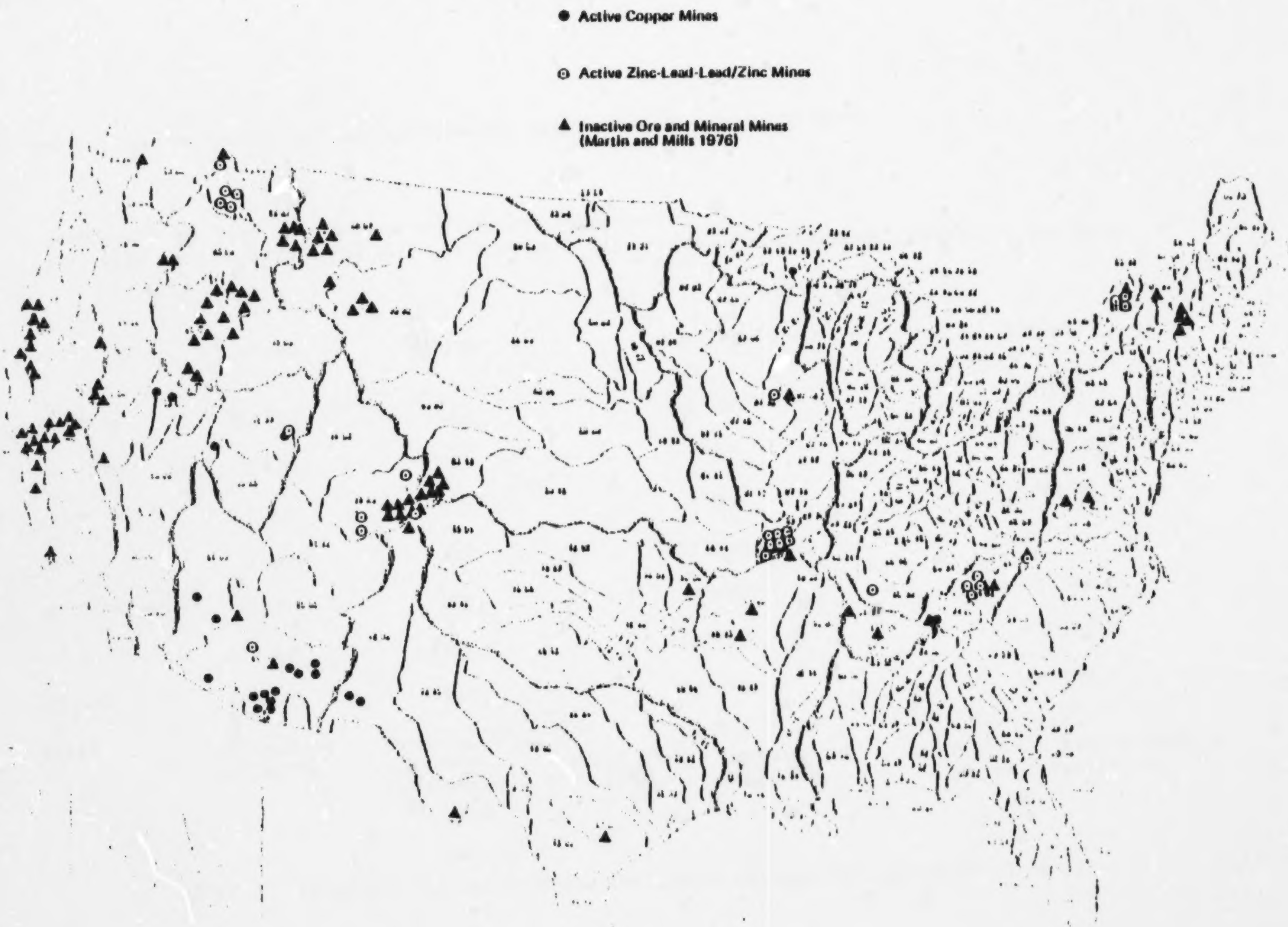

● Active Copper Mines
⊙ Active Zinc-Lead-Lead/Zinc Mines
▲ Inactive Ore and Mineral Mines (Martin and Mills 1976)

FIGURE 3. LOCATION OF ACTIVE AND INACTIVE MINES IN THE UNITED STATES

TABLE 3. ESTIMATED COPPER RELEASES FROM MINING AND MILLING ACTIVITIES, 1978

State	Ore Mined (1000 MT/yr)	Concentrate Produced (1000 MT/yr)	Copper Deposited as Solid Wastes from Milling (MT/yr)	Copper Deposited as Solid Wastes from Mining (MT/yr)
Arizona	159,769	2,179[1]	126,310	399,900
Nevada	16,362	253[1]	21,420	63,750
New Mexico	21,323	421[1]	21,600	122,700
Utah	32,208	753	21,980	169,050
Tennessee	1,836	853	1,000	negligible
Michigan	3,281	125	1,280	negligible
Montana	15,419	327	15,100	114,200
Total	250,198	4,911+	208,690	869,600

[1] Indicates that certain mills have not published production of concentrate; therefore, the above quantities are less than actual concentrate production.

Source: Arthur D. Little, Inc., estimates, 1979, based on EPA NPDES data.

Washington (EPA, 1977b). The smelting process applies sufficient heat to the copper ore/concentrate to convert the gangue into a slag (waste product) and simultaneously to concentrate the copper into a high grade material. It involves the processes of roasting, reverbatory smelting, converting and fire refining. The copper is formed as a matte containing 30% to 70% copper (NIOSH, 1975). The matte is oxidized to remove iron and sulfur by streams of hot air forced through the molten mass.

Studies of the atmosphere surrounding copper smelters in Utah, Arizona, and Montana revealed moderate to high concentrations of copper (NIOSH, 1975). Quantification of the material released in terms of bulk discharge per unit production is difficult, however, because these studies were conducted to determine human exposure levels rather than rates of emission. As with mines and mills, western smelters must operate within constraints of a limited water supply and are likely to recycle water used. Even including releases from the two non-western smelters, aquatic discharges from smelters are expected to be negligible.

Secondary copper production involves the direct electrowinning and refining from scrap metal. Data (for 1976) obtained from effluent guidelines monitoring at EPA (Versar, 1979) indicate that 0.3 MT are discharged directly to water annually and 7 MT to POTW's annually. It is thought that atmospheric emissions of copper from secondary production are small (Arthur D. Little, Inc., estimates).

2. Production in Which Copper is a Byproduct/Contaminant

In addition to the copper mines, relatively small quantities of copper are found in the effluents of lead-zinc mines. The majority of these are located in the five states of Missouri, Tennessee, Idaho, New York, and Colorado. The amount of copper released from this source is estimated to be 5.7 MT annually (Arthur D. Little, Inc., estimates). Copper is also present in the effluents from various other ore mines, and is estimated to amount to a release of 1.9 MT annually.

Copper appears in the ash of most coals in trace amounts; consequently coal combustion should provide a release of copper to the atmosphere. Reliable documentation quantifying this emission is not readily available; however, for a 99.5% recovery of coal ash and given the extremely low concentrations of copper in coal, this release is not expected to be significant.

Copper also appears as an impurity in materials used in the production of iron and steel and subsequently 17 MT annually is emitted to the atmosphere and 896 MT is disposed of on land. This approximation is determined by the efficiencies of pollution controls on iron and steel production processes (Arthur D. Little, Inc., estimate).

TABLE 4. POTENTIAL ENVIRONMENTAL RELEASE OF ELEMENTAL COPPER RELATED TO AGRICULTURE, 1976

Region[1]		Fungicides Copper/Sulfate (MT/yr)	Fungicides Other Coppers[2] (MT/yr)	Algicides Copper Sulfate (MT/yr)	Wood Preservatives Other Coppers[1] (MT/yr)	Discharge of Copper Through Impurities and Adjuvants in Fertilizers (MT/yr)
Northeast		78	31	(Not Available by Region)	500	(Not Available by Region)
Appalachian		1,157	-			
Southeast		3,471	253		3,500	
Lake States	North Central	35	-			
Corn Belt		1,871	143		900	
Northern Plains		9	-			
Delta States	South Central	-	-		1,100	
Southern Plains		9	-			
Mountain		-	-		600	
Pacific		2,070	573		800	
Total		8,700	1,000	3,600	8,000	1,336 - 1,654

[1] Agricultural production regions apply except for wood processing regions; both are defined in Figure 3.
[2] Copper oxychloride sulfate, copper hydroxide, cuprous oxide, copper oleate, copper, chromated copper arsenate, and acid copper chromate.

Source: USDA (1974); EPA (1974); SRI (1979).

Probably as a naturally occurring constituent, copper has been detected in discharge waters from the pulp and paper industry and the steam electric industry. These two sources discharge 110 MT and 174 MT, respectively, each year directly to waters (EPA, 1979).

3. Environmental Release of Copper During Manufacturing Processes and Consumptive Use

Of the 2.4 million MT consumed in the U.S. in 1976, over 99% was used in the pure metallic form or in alloys that are predominantly copper (Versar, 1978). Manufacturing uses of copper include the wire mills and brass mills.

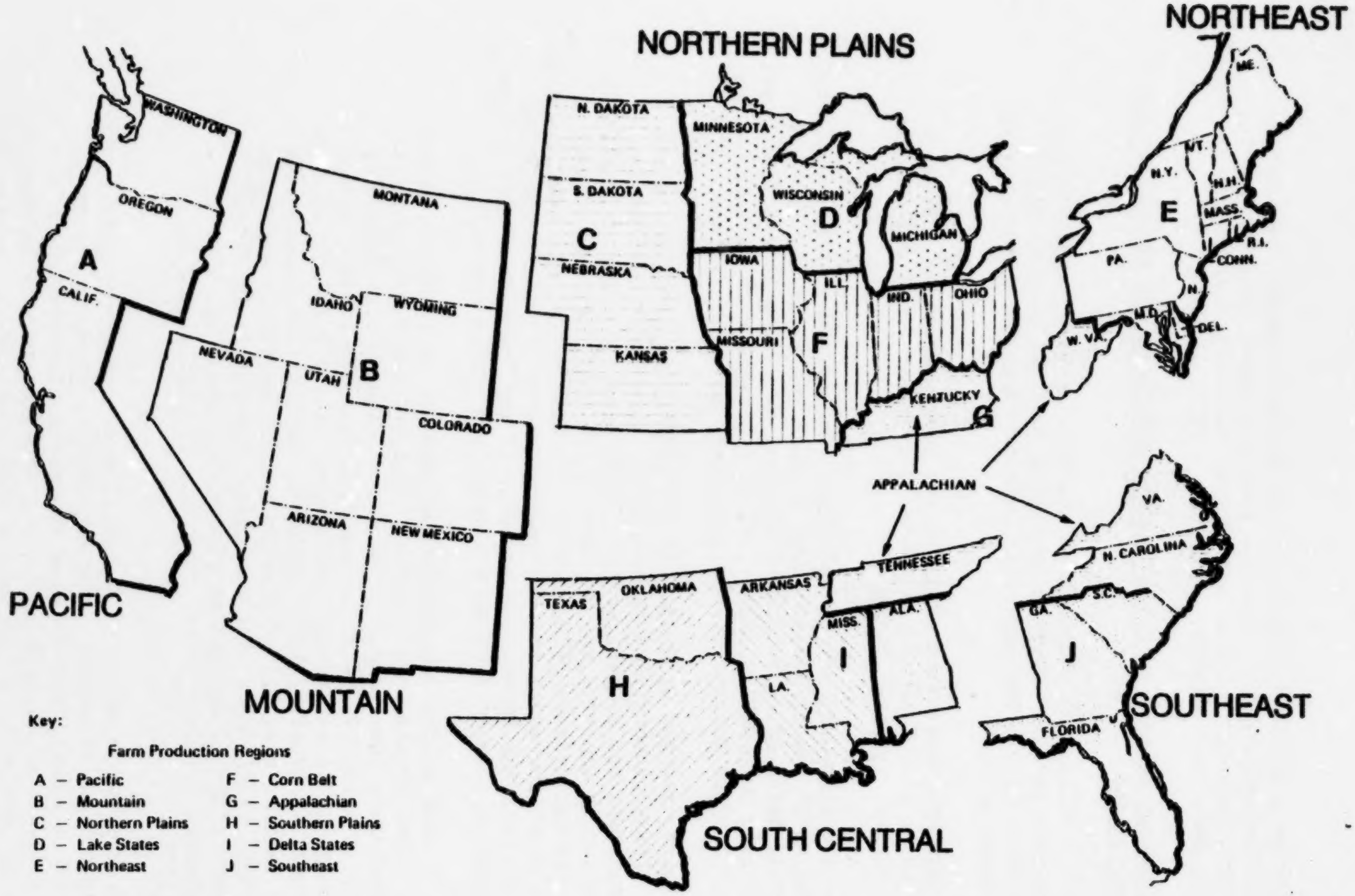
Based upon EPA monitoring data, it has been determined that wire mills contribute 164 MT to air and 1618 MT to water (POTW and direct aquatic) annually (Versar, 1978).

Brasses are alloys of copper and zinc. The Bureau of Mines estimated that 567,000 MT of copper was consumed by this use in 1976. Based upon EPA monitoring data, it is estimated that 445 MT of copper are discharged to water (direct and POTW) annually, 42 MT is disposed of as solid waste annually and 3 MT is emitted to the atmosphere annually (Versar, 1979).

The largest consumer of copper is the electrical industry, which uses it in wiring, communications equipment, electronic components, lighting equipment and in generators. Because of its superior qualities of high conductive capacity and relatively low corrodibility, copper is used in the manufacture of electrical components that are intentionally shielded from environmental interference to ensure efficient operation. Consequently, pathways to the environment, if any, involve a slow process, and environmental release from this consumptive use is negligible.

Copper is used in the electroplating industry in a modest amount relative to other metals, e.g., nickel. The process by which it is consumed discharges some copper to water. Estimated consumption by the industry is about 27,200 MT of copper a year (Schroeder, 1979). Conservatively, it is estimated that no more than 10% is released to the environment (Schroeder, 1979; Arthur D. Little, Inc., estimates, 1979). EPA reports that 52% of electroplating operations discharge to POTW's (EPA, 1979). From the remainder, approximately 70% of waste is treated and discharged as sludge, and the other 30% is effluent released directly to water (Arthur D. Little, Inc., estimates, 1979).

The construction industry is a significant consumer of copper; its uses include roofing materials, heat exchangers, plumbing, tubing, valves and process equipment. Copper exposed to the atmosphere -- such as in roofing, drainage gutters, and exterior trim -- is naturally susceptible to acid rains and oxidation and, consequently, erodes more rapidly. Copper used in plumbing, valves and tubing is routinely


NORTHERN PLAINS
NORTHEAST
PACIFIC
MOUNTAIN
SOUTH CENTRAL
SOUTHEAST
APPALACHIAN
A
B
C
D
E
F
G
H
I
J
WASHINGTON
OREGON
CALIF.
MONTANA
IDAHO
WYOMING
NEVADA
UTAH
COLORADO
ARIZONA
NEW MEXICO
N. DAKOTA
S. DAKOTA
NEBRASKA
KANSAS
MINNESOTA
WISCONSIN
MICHIGAN
IOWA
ILL.
IND.
OHIO
MISSOURI
KENTUCKY
ME.
VT.
N.H.
N.Y.
MASS.
R.I.
CONN.
PA.
N.
M.D.
DEL.
W. VA.
VA.
N. CAROLINA
S.C.
GA.
FLORIDA
TENNESSEE
TEXAS
OKLAHOMA
ARKANSAS
LA.
MISS.
ALA.
Key:
Farm Production Regions
A – Pacific
B – Mountain
C – Northern Plains
D – Lake States
E – Northeast
F – Corn Belt
G – Appalachian
H – Southern Plains
I – Delta States
J – Southeast

Source: Arthur D. Little, Inc. from USDA 1974; SRI, 1979.

FIGURE 4. WOOD PROCESSING REGIONS OF THE UNITED STATES
(Data Excludes Alaska and Hawaii)

exposed to moisture and is likely to be released to the aquatic environment. Although the nature and quantities of these industrial applications are fairly well defined, consequent release to the surrounding environment is less predictable.

Copper is consumed in the machinery industry in the production of mining machinery, conveyors, bushings, bearings, and miscellaneous tools. The transportation industry uses copper in radiators, carburetors, tubes, and brakes. This latter application contributes an unquantified amount of copper to roadways and thus is potentially a source of copper in urban runoff.

There are several other industries in which copper was detected but all discharged minor amounts ($\leq$ 10 MT annually). These include: printing and publishing, ore mining, textiles, non-ferrous metals, rubber, petroleum refining, leather tanning, gum and wood chemicals, inorganic chemicals, and paint and ink. Automatic and other laundries discharged 82 MT per year to POTW. (EPA, 1979).

Copper sulfate is a chemical compound that has long been used in agriculture. The U.S. Department of Agriculture (USDA) recommends copper sulfate as the safest, most effective, inexpensive, and extensively used algicide (EPA, 1974); this copper enters the aquatic environment directly. Other agricultural uses include in fungicides, feeds, and fertilizers on citrus fruits, deciduous fruits, and vegetables. Copper sulfate is also used in industry to froth flotation agents and supplement wood preservatives. Table 4 and Figure 4 summarize agricultural consumption of copper sulfate by regions, where available, based on 1971 and 1974 data from USDA and in a study for EPA by SRI (1979). Most of these uses have, by definition, entered the environment (the soil compartment) upon their use. The use of copper as a wood preservative does not reach the environment immediately, although it would eventually reach the soil compartment. We have assumed that the use of this product has been similar in the past, and thus releases have achieved equilibrium. Chromated copper arsenate is used as a wood preservative to treat lumber and timbers, primarily Douglas Fir and Southern Pine (SRI, 1979).

Copper exists as an impurity in phosphate rock from which phosphatic fertilizers are produced. In a study of agriculture-related releases of copper (1979), SRI determined that between 136 MT and 454 MT of elemental copper are discharged annually. Because of the nutritional requirements of plants and animals for copper, copper is used as an adjuvant in fertilizers. In the above study, SRI determined that approximately 1200 MT of copper are used each year for this purpose.

4. Other Sources

The iron and steel industry represents a major source of copper, especially to the aquatic environment. Versar (1980) has estimated that this industry releases 656 MT to water annually, based on data from Effluent Guidelines Division.

Copper is a natural constituent of the soil at concentrations ranging from 1 mg/kg to 50 mg/kg. Consequently, copper resulting from soil runoff is transported in streams and water bodies throughout the United States. The average annual total suspended load of the United States has been estimated by Wischmeier (1976) as 3.6 billion MT, 25% of which enters the major streams. If a copper concentration of 20 mg/kg is assumed, approximately 18,000 MT of copper is discharged to water via this route. Obviously, a large part of this is a result of cultural activities, such as agriculture and construction. However, some of it is due to natural background weathering.

Urban runoff receives a substantial quantity of copper from a variety of identifiable sources. Possible sources of copper release in the urban/industry environment include exposed construction elements (roofing, gutters and trim), transportation (radiators, carburetors, brakes, etc.) and industrial applications (plumbing, tubing, valves, etc.), as discussed above. Assuming a concentration of 25 ug/l in urban runoff (EPA 1980) and a volume of 21×10^{12} l/yr (EPA 1977c), a release of 525 MT/yr can be estimated. The major portion (441 MT) flows to separate storm sewers (41%) (point sources) and to unsewered areas (43%) (non-point sources). Combined sewers contribute the remaining 16% (84 MT) to POTW's. As shown in Table 2, total urban runoff must be considered one of the major sources of pollutant loading.

Environmental release of copper during its production processes is partially regulated by EPA guidelines. Mining operations dispose of tailings at controlled land areas at or near the mine site. The copper is locked in silicate compounds or other insoluble forms, and this decreases the likelihood of leaching. Release of copper to the air and water is minimized by two significant factors. First, the relatively high cost of copper in the current industrial market makes it economically attractive to recover the maximum amount of the metal in bag houses and other related mechanisms; this provides the primary incentive for reducing air emissions of copper. Second, most copper mining operations are located in the Midwest and Southwest portions of the United States. These areas are characteristically dry regions in which water is at a premium; consequently, there is little if any discharge of waters from the operations. Four exceptions exist; they are located in Michigan, Montana, Tennessee and Utah. However, abandoned mines and past disposal practices can result in significant discharges to the environment. Figure 3 shows the numerous locations where such situations exist, although the map includes all abandoned mines. Martin and Mills (1976) have estimated that 314 MT reach the aquatic environment annually as a result of abandoned mines.

POTW's also represent a significant source of copper to the environment. Influents and effluents indicate an abnormally high concentration of copper in streams located near industrial areas (EPA, 1979). Because no other apparent source of copper release exists, these copper concentrations must be attributable to urban runoff, industrial discharge, and domestic and commercial areas.

In this study, the available data have been examined and an estimate made on the basis of a flow-weighted mean concentration of copper in POTW influent and on mean removal efficiencies of primary and secondary treatment plants.

A substantial number of studies addressing the composition of POTW influent and effluent have been accomplished in recent years. Many of the individual studies are of a single POTW and there is considerable variability in the nature of the study, the quality of the reporting, and the indicated range of values for copper concentration. Several studies present data and conclusions based on groups of POTW's that were investigated. Table 5 indicates the range of results reported. Of the studies examined, none presents data from a truly representative cross section of POTW's in the United States. However, one (Sverdrup and Parcel, 1977) presents a relatively consistent data set on 103 POTW's clustered mainly in the Midwest, with some additional plants in California, New Jersey, New York, and elsewhere in the Southeast. The authors of the Sverdrup and Parcel study concluded that their data describe "typical" POTW's with regard to heavy metals. Since the study emphasized secondary treatment plants, only a small number of primary plants are represented in the sample. With data presented in the study, a flow-weighted mean concentration, $\bar{C}$, for copper concentration in the influent of the 103 POTW's was calculated by the following formula:

$$\bar{C} = \frac{\Sigma^{103} C_i V_i}{\Sigma V_i} = 250\ \mu g/l$$

Where:

$\bar{C}$ = concentration of i^{th} POTW

V_i = flow volume of i^{th} POTW

The Sverdrup and Parcel report concluded that POTW's meeting secondary treatment standards removed an average of 82% (range from 55% to 90%) of the copper in the influent. This conclusion is drawn from data on 22 of the 103 plants that met these standards and for which sufficient data existed on all parameters of interest.

TABLE 5. REPORTED COPPER CONCENTRATIONS IN POTW INFLUENT

POTW's	Land Use	Values Reported (mg/l)
12 - New York City[1]	Residential	Mean = 0.21
99 - New York, New Jersey & Connecticut[2]	Mixed	50% below 0.10 95% below 0.85 100% below 9.60
10 - Southern Ontario[3]	Mixed	50% below 0.15 90% below 0.35 100% below 1.20
103 - United States[4]	Mixed	Median = 0.12 Range = 0.01 - 1.968
12 - New York City[5]	Mixed	$\bar{x}$ = 0.238 (0.13 - 0.43)
6 - New York City Sewers[5]	Residential	$\bar{x}$ = 0.202 (0.11 - 0.33)

[1] Davis and Jacknow, 1975.
[2] Mytelka *et al.*, 1973
[3] Oliver and Cosgrove, 1975.
[4] Sverdrup and Parcel Associates, 1977 draft.
[5] Klein *et al.*, 1972.

Sverdrup and Parcel (1977) noted that while influent concentrations reported elsewhere in the literature agreed with their data, the removal efficiencies reported elsewhere tended to be lower. They suggested that the explanation could be that other analyses included some POTW's not meeting secondary treatment standards. In any event, 82% was both the median and flow-weighted mean of the removal efficiencies for the 22 plants. Data were presented on removal efficiency for 10 primary treatment facilities in addition to the 22 secondary plants. The median value of removal efficiency for the primary plants was 37% while the flow-weighted mean was 31%. The latter was used in the above calculations to estimate partitioning between sludge and release to the aquatic environment.

Data on improved metals removal during advanced treatment are sparse. However, it was assumed that an improvement of 3% over secondary treatment could be achieved. Therefore, advanced treatment was assumed to be capable of removing 85% of the copper in the influent.

The total amount of treated effluent from POTW's in the United States and outlying territories is estimated to be 34,031 MGD on the basis of the 1976 needs survey as reported by SRI International (R. A. Marshall, 1978 a,b). It is also estimated from this report that less than 2% of the flow is from primary treatment plants, while nearly 64% undergoes secondary treatment, and nearly 35% undergoes advanced treatment.

Table 6 summarizes the POTW copper budget on the basis of the above assumptions and shows that 2073 MT of copper is discharged by POTW's to the aquatic environment, while 9680 MT is discharged to land.

Identifying the source(s) of copper observed in POTW's remains problematic. Only 2341 kkg of copper released to POTW's are accounted for in Table 2. Recent studies (Arthur D. Little, Inc., 1979) have shown that residential areas are significant sources of copper in the sewer systems of Cincinnati and St. Louis. Data from these two cities suggest that copper loadings of 26.3 - 57.7 mg/day/person may be generated by residential areas. For an average of 42 mg/day/person, the total copper loading to POTW's from all residential area sources would be 3066 MT, leaving 6347 MT of the POTW's loading to be accounted for by industrial and natural discharges.

5. Copper Disposal

Little information is available on levels of copper in refuse. However, it is likely that copper does comprise some small portion of municipal solid waste, about 5% of which is incinerated. Some portion (probably much less than one-half) of the copper in the incinerated waste would be released to air, while the remainder would to go ash and be discharged to land. If 0.001% of the 1979 municipal solid waste load of 200 million MT in the United States is assumed to be copper,

TABLE 6. SUMMARY OF POTW COPPER BUDGET

	Flow (MDG)	Copper Loading(L) to POTW (kkg)[1]	Treatment Removal Efficiency	POTW Discharge (kkg) To Sludge	POTW Discharge (kkg) To Water
1976 Needs Survey					
Primary Treatment	336	116	.31[2]	36	80
Secondary Treatment	16,019	5,533	.82[2]	4,537	996
Advanced Treatment	8,711	3,008	.85[3]	2,557	451
Total	25,066	8,657		7,130	1,527
Flow not included in Needs Survey	8,965	3,097		2,550	546
Total flow treated by POTW in U.S. and outlying territories	34,031	11,754		9,680	2,073

[1] $L(\text{kkg/yr}) = \text{flow (MGD)} \times 250\ (10^{-6}\text{g/l}) \times 3.785\ (\text{l/gal}) \times 365\ (\text{day/yr}) \times 10^{-6}(\frac{\text{kkg}}{\text{g}}) = 0.3454 \times \text{flow}$.

[2] Flow-weighted mean value calculated from Sverdrup and Parcel Associates data, February 1977.

[3] Assume advanced treatment removes Cu proportionately to TSS--estimated 3% increment from SRI, September 20, 1978.

Source: Derived from 1976 Needs Survey, reported by SRI International (1978 a,b).

then 2,000 MT of copper would be in the waste (Arthur D. Little, Inc., estimate). Incineration would release a maximum of 100 MT to the air and the remaining 1,900 MT would be disposed of on land, either directly with the municipal solid waste or as ash remaining after incineration. Most of this waste would be in metallic form.

A study published on the subject of municipal wastes reports copper occurring at concentrations as high as 0.16% in solid waste (NAS, 1975). Assuming the above waste load, this would signify 320,000 MT of copper in this source, of which 16,000 MT goes to air by incineration and the remaining 304,000 MT is deposited to land. This estimation is presented as an alternative though we feel that it may be unreasonably high. The state of knowledge in the area of municipal waste is currently poorly documented and considerable further work is needed.

C. Summary

Copper is released to all environmental compartments as illustrated in Table 2. The most significant receptor is land, to which *in situ* mining operations, agricultural activities, and POTW sludge disposal are the three largest contributors. Mining contributes by far the largest quantity in the form of mining and milling wastes. The copper in these wastes is in a chemically bound form with little, if any, potential for further release to the environment. Agricultural preparations containing copper are distributed at recommended concentrations designed to fulfill functions as pesticides, nutrients, etc. POTW sludge accounts for less than one-half of the amount used in agricultural applications.

The water compartment receives most of its copper initially from three major sources: suspended sediment, POTW's, and agricultural application. POTW loadings represent more localized releases, while soil runoff and agricultural sources represent non-point sources. Various industries also account for additional small direct contributions to water but, as shown in Table 2, the identified industries account for only 9% of the direct aquatic release. However, they may represent important sources in local areas. In addition, abandoned mines represent a source of copper to the aquatic compartment. These sources may, however, contribute significantly to the copper levels in very local environments.

Airborne releases are apparently very small and the major ones are associated with copper wire mills and, hence, are very localized.

REFERENCES

Arthur D. Little, Inc. 1979. Sources of toxic pollutants found in influents to sewage treatment plants. VI. Integrated Interpretation, Part 1. Report on EPA Contract No. 68-01-3857.

Bureau of Mines. 1977. Minerals Yearbook 1977. Copper. Washington, D.C.

Council for Agricultural Science and Technology. 1976. Application of sewage sludge to cropland-appraisal of potential hazards of heavy metals to plants and animals. Ames, Iowa. (EPA #PB-264-015).

Davis, J. and J. Jacknow. 1975. Heavy metals in wastewater in three urban areas. JWPCF 47(9):2292.

Klein, L.A., M. Long, S. Nash and S.L. Kirschner. 1974. Sources of metals in New York City wastewater. Metal Finishing. 34:5.

Martin, H.W. and W.R. Mills, Jr. 1976. Water pollution caused by inactive ore and mineral mines - a national assessment. NTIS # PB-264-936. Prepared for the Office of Research and Development, EPA, Cincinnati, OH.

Mytelka, A., J.S. Crachoe, W.B. Guggino and H. Golub. 1973. Heavy metals in wastewater and treatment plant effluents. JWPCF 45:1859-1864.

National Academy of Sciences. 1975. Mineral resources and the environment, supplementary report. Washington, D.C.

National Institute for Occupational Safety and Health (NIOSH). 1975. Environmental conditions in U.S. copper smelters. Cincinnati, OH.

National Research Council. 1977. Zinc. National Academy of Science. Baltimore: University Park Press.

Oliver, B.G. and E.G. Cosgrove. 1975. Metal concentrations in the sewage effluents and sludges of some southern Ontario wastewater treatment plants. Env. Letters 9(1).

Schroeder, H.J. 1979. Bureau of Mines, Metals Section. Personal communication.

Sittig, Marshall. 1975. Environmental Sources and Emissions Handbook. Park Ridge, New Jersey: Noyes Data Corporation.

SRI International (Robert A. Marshall). 1978a. Toxic survey for publicly owned treatment plants (draft final report) - Task 3 under EPA Contract 68-01-3887.

SRI International (Robert A. Marshall). 1978b. Statistical support for analytical survey of publicly owned treatment plants (draft final report, Part 1) - Task 4 under EPA Contract 68-01-3887.

SRI International (S.E. Casey). 1979. Agricultural sources of zinc. Draft report to the Monitoring and Data Support Division, EPA.

Sverdrup & Parcel and Associates, Inc. 1977. Study of selected pollutant parameters in publicly owned treatment works (draft) - Task Order No. 7 under EPA Contract 68-01-3289.

United States Department of Agriculture. 1974. Farmers' use of pesticide in 1971. Washington, D.C.

United States Environmental Protection Agency. 1972. AP-42 compilation of air pollutant emission factors. Washington, D.C.

United States Environmental Protection Agency. 1974. Production, distribution, use and environmental impact potential of selected pesticides. Washington, D.C.

United States Environmental Protection Agency. 1977a. State and local pretreatment programs (federal guidelines). Washington, D.C.

United States Environmental Protection Agency. 1977b. Heavy metal pollution from spillage at ore smelters and mills. Washington, D.C.

United States Environmental Protection Agency. 1977c. Nationwide evaluation of combined sewer overflows and urban stormwater discharges, Volumes I and II. Washington, D.C.

United States Environmental Protection Agency. 1979. Effluent guidelines data, as yet unpublished. Effluent guidelines division, Office of Water Planning and Standards. Washington, D.C.

United States Environmental Protection Agency. 1980. Memo to Jody Perwak, Urban Runoff Pollutants, Charles Delos, Monitoring and Data Support Division. Jan. 11, 1980.

Versar, Inc. 1978. Materials balance: Copper. Draft report to the Monitoring and Data Support Division, EPA.

Versar, Inc. 1979. Effluent guidelines monitoring data. Memo to Monitoring and Data Support Division, EPA.

Versar, Inc. 1980. Effluent guidelines monitoring data. Memo to Monitoring and Data Support Division, EPA.

Wischmeier, W.H. 1976. Cropland and erosion and sedimentation. Control of Water Pollution from Cropland Vol. II. Agricultural Research Service, USDA, Washington, D.C.

SECTION IV.

DISTRIBUTION OF COPPER IN THE ENVIRONMENT

A. MONITORING DATA

1. Copper in Water

STORET data provide the most complete survey of ambient concentrations of copper in freshwater. This discussion focuses on levels of total, rather than dissolved copper primarily because dissolved copper was infrequently measured.

The nationwide distribution of observations of total aqueous copper is as follows:

- 4% of all samples are in the range of .1 µg/L to 1 µg/L;
- 41% are between 1 µg/L and 10 µg/L; and
- 44% fall into the 10 µg/L to 100 µg/L category;
- 10% are between 100 µg/L and 1,000 µg/L; and
- 1% exceed 1 mg/L.

This distribution is depicted graphically in the histogram in Figure 5. Table 7 lists all of the major river basins and the distributions of concentrations for each. The major river basins with the highest total concentrations of aqueous copper (i.e., those with the greatest percentage of samples containing concentrations in excess of 100 µg/L) are the New England, Western Gulf, and Lower Colorado River basins (see Table 26 in Section VII).

STORET data indicate that bottom sediments in rivers normally contain between 1 mg/kg and 1,000 mg/kg of copper, which is two to four orders of magnitude greater than concentrations found in river water. The distribution of values is: 30% of observations between 1 mg/kg and 10 mg/kg 60% between 10 mg/kg and 100 mg/kg; and 8% between 100 mg/kg and 1,000 mg/L. The regions with the highest concentrations in sediment are Hawaii, the Lower Colorado River basin, and Upper Mississippi Valley, and the Great Lakes (see Table 8 and Section VII).

An extensive search of the literature for levels of copper in seawater was not conducted, however, most reports of copper concentrations in seawater are in the range of 1-5 µg/l (Friberg *et al.*, 1977).

Preceding page blank

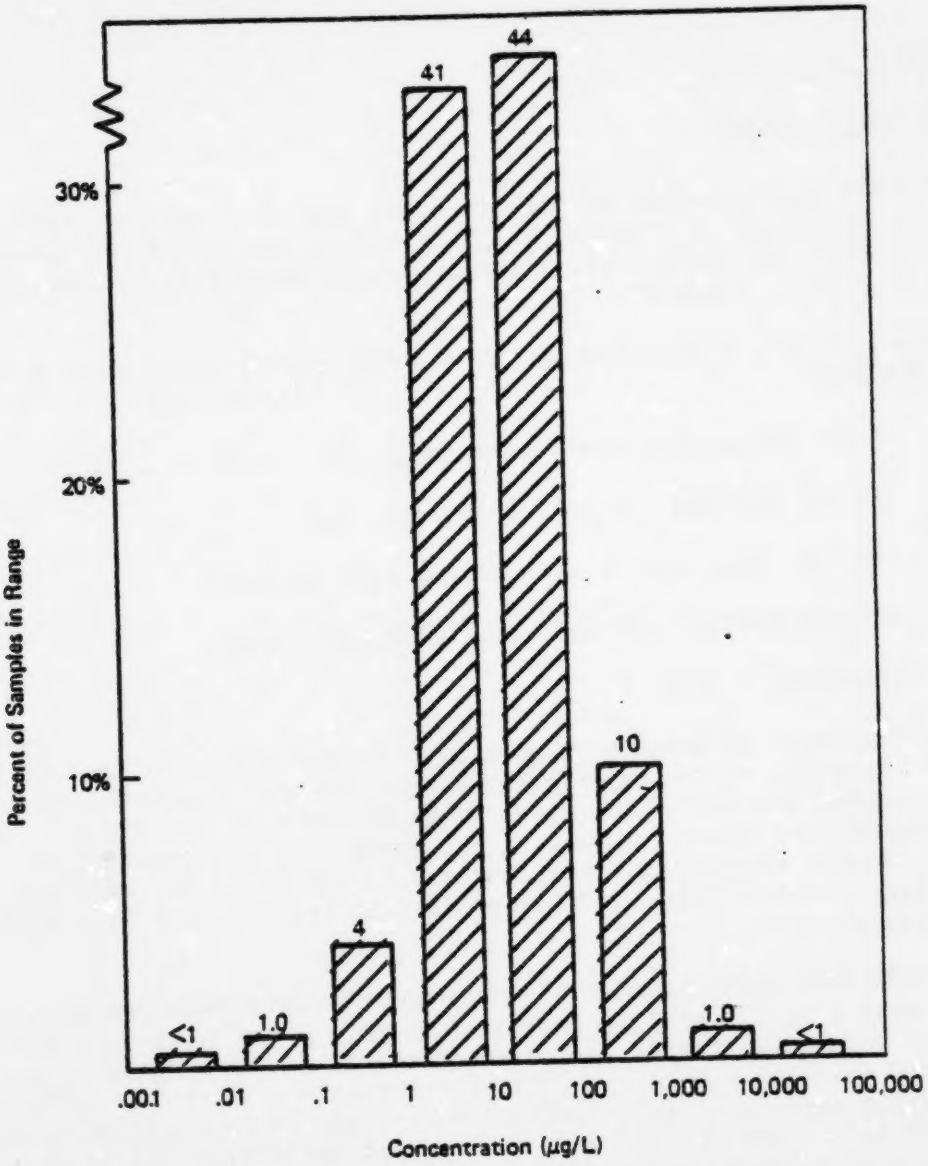


FIGURE 5. DISTRIBUTION OF TOTAL COPPER IN U.S. RIVER BASINS

TABLE 7. TOTAL COPPER IN AMBIENT WATERS BY REGION, 1970-1979

Region	Percentage of Observations				
	.100-1 μg/L	1-10 μg/L	10-100 μg/L	100 μg/L-1000 μg/L	1000-10,000 μg/L
New England	3	40	33	18	4
Mid Atlantic	1	38	49	9	1
Southeast	2	43	37	16	1
Great Lakes	1	45	48	5	<1
Ohio	1	44	49	5	1
Tennessee	<1	32	58	9	1
Upper Mississippi	<1	33	44	12	9
Souris and Red of North	<1	36	62	2	<1
Missouri	<1	44	49	6	<1
Arkansas and Red	1	45	43	11	<1
Western Gulf	3	47	29	18	<1
Hawaii	1	58	33	5	<1
Rio Grande and Pecos	9	43	34	12	2
Upper Colorado	<1	57	35	6	1
Lower Colorado	2	23	39	33	2
Great Basin	<1	48	44	8	<1
Pacific Northwest	3	55	35	6	<1
California	1	38	52	7	2
Alaska	2	48	44	6	<1
United States	4	41	44	10	1

Source: U.S. EPA, 1979c.

TABLE 8. TOTAL COPPER IN SEDIMENTS IN U.S. REGIONS, 1970-1979

Region	Percentage of Observations			
	1-10 mg/kg	10-100 mg/kg	100-1,000 mg/kg	1,000-10,000 mg/kg
New England	33	50	15	1
Mid Atlantic	31	53	15	<1
Southeast	41	56	1	<1
Great Lakes	14	65	17	2
Ohio	24	73	4	<1
Tennessee	20	69	10	1
Upper Mississippi	23	58	4	15
Lower Mississippi	24	72	2	<1
Souris and Red of North	24	41	<1	35
Missouri	54	39	7	<1
Arkansas and Red	57	43	<1	<1
Western Gulf	37	59	2	<1
Hawaii	<1	33	67	<1
Rio Grande and Pecos	16	84	<1	<1
Upper Colorado	53	46	1	<1
Lower Colorado	40	40	20	<1
Great Basin	-	-	-	-
Pacific Northwest	14	81	5	<1
California	18	75	7	<1
Alaska	-	-	-	-
United States	30	60	8	1

Source: U.S. EPA 1979c.

2. Copper in Aquatic Organisms

The amount of copper in the tissues of aquatic organisms is dependent upon both concentration in water and dietary intake.

The most comprehensive compilation of data on copper residues in fish tissues is in STORET. Of 1,150 residue analyses performed throughout the U.S. (mostly in freshwater organisms), 67% contained from 1 mg/kg to 10 mg/kg copper, and 27% had concentrations between 10 mg/kg and 100 mg/kg. The regions in which the mean copper residues were highest are Hawaii, Puerto Rico, and the Colorado River Basin. Fish in the Western Gulf states also showed high residues, however, sampling was limited.

NRC (1977) summarized a number of studies reporting copper concentrations in the edible portions of marine fish, ranging from 1 mg/kg for cod to 36 mg/kg for oysters. In one study, the Atlantic oyster (Crassostrea virginica) had copper concentrations as high as 1,050 mg/kg when exposed to water with 50 µg/L copper (Shuster and Pringle, 1969, as cited in Phillips and Russo, 1978). As a group, mollusks have copper residues of 1.24-1,050 mg/kg. Various species of marine worms have concentrations ranging from 5.96 mg/kg to 84.4 mg/kg copper. Ten species of freshwater fish found in the Illinois River had copper residues of 0.05 mg/kg to 0.39 mg/kg. No significant differences in the residues of omnivorous and carnivorous fish were apparent. These data are listed with references in Table 9.

3. Copper in Plants

Copper is an essential micronutrient for the normal growth and development of green plants. Although the quantitive requirements of plants are lower than for any other nutrient except molybdenum, there are many documented cases of naturally occurring copper deficiency. Copper toxicosis, on the other hand, is rarely observed except on tailing dumps or where fertilizers or fungicides high in copper have been used extensively (NRC, 1977).

Copper concentrations in edible plants range from 1 mg/kg to 143 mg/kg (NRC, 1977). Allaway (1974) gives the range as 4-15 mg/kg on a dry weight basis. Crops with high copper requirements for optimal productivity include wheat, barley, oats, corn, carrots, red beets, onions, spinach, alfalfa, and cabbage (in decreasing order of importance). Fink *et al*. (1976) examined ten species of freshwater plants, and found copper concentrations of 2.5-65.5 mg/kg.

Much of the copper in soils is not available for plant uptake except in acidic soils. Liming soils to pH 7 or 8 reduces copper availability and may be a factor in some areas where plants are copper-deficient (NRC, 1977).

TABLE 9. RESIDUES OF COPPER IN AQUATIC ORGANISMS

Species	Concentration (mg/kg)	Reference
Polychaete (*Cirriformia spirabrancha*)	5.96-69.81	Milanovich *et al*. (1976)
Squid (3 sp.)	15,000 (max.)	Martin and Flegal (1975)[1]
Various mollusks	1-10	Marks (1938)[1]
Bloodworm (*Glycera dibranchiata*)	10.1-28.0	Fink *et al*. (1976)
Bristleworm (*Nephthys* sp.)	8.9	Fink *et al*. (1976)
Clamworm (*Nereis diversicolor*)	0.8-84.4	Fink *et al*. (1976)
Sandworm (*Nereis virens*)	12.1-15.6	Fink *et al*. (1976)
Common Periwinkle (*Littorina littorina*)	54.6-68.0	Fink *et al*. (1976)
Blue Mussel (*Mytilus edulis*)	3.9-8.5	Fink *et al*. (1976)
Soft Shell Clam (*Mya arenaria*)	8.4-21.5	Fink *et al*. (1976)
Clam (*Macoma balthica*)	88.1-171	Fink *et al*. (1976)
Northern Pike (*Esox lucius*)	0.05-0.08	Mathis and Cummings (1973)
Largemouth bass (*Micropterus salmoides*)	0.08-0.13	Mathis and Cummings (1973)
(*Morone chrysops*)	0.17-0.24	Mathis and Cummings (1973)
Shortnose Gar (*Lepisosteus platostomus*)	0.13-0.20	Mathis and Cummings (1973)
Black Bass (*Micropterus dolomieui*)	0.14-0.16	Mathis and Cummings (1973)
Bigmouth Buffalofish (*Ictiobus cyprinellus*)	0.07-0.26	Mathis and Cummings (1973)
Gizzard Shad (*Dorosoma cepedianum*)	0.18-0.39	Mathis and Cummings (1973)
Redhorse (*Moxostoma macrolepidotum*)	0.16-0.20	Mathis and Cummings (1973)
Quilback Carpuckers (*Carpiodes cyprinus*)	0.10-0.30	Mathis and Cummings (1973)
Carp (*Cyprinus carpio*)	0.12-0.41	Mathis and Cummings (1973)

---

[1] As cited in Phillips and Russo (1978)

4. Copper in Soil

Copper occurs naturally at a concentration of approximately 50 mg/kg in the earth's crust, which includes both parent rock and soil. Of the parent materials, biotite and pyroxene basalts have the highest copper concentrations, averaging 140 mg/kg. Ranges in copper concentration of 10-40 mg/kg are commonly found in sandstone, Copper is normally found only in relatively low concentrations in coal. Copper tends to be concentrated in clay mineral fractions, with some further enrichment in clays with high organic carbon content. It is also concentrated in manganese oxides where levels up to 0.1% have been found (NRC, 1977).

The rate at which parent rock is degraded into the derivative soil depends upon the pH, the redox potential, the amount of organic matter in existing soil, the mechanism of formation of the derivative soil, and the degree of weathering. The pH is of particular concern in agriculture because copper is more mobile (in dissolved form) under acid than under alkaline conditions (NRC, 1977).

Ambient copper concentrations found in soils are approximately 20 mg/kg. In agriculturally productive soils, copper occurs in a range of 1-50 mg/kg. Soils derived from mineralized parent material often have much higher values (NRC, 1977).

5. Copper in Air

a. Work Environment

The OSHA standard for airborne copper in a work environment is 1.0 mg/m^3 (a time-weighted average for 8-hr daily exposure to copper dust). The standard for copper fume is 0.2 mg/m^3, (NRC, 1977).

b. Non-work Environment

A range of 0.01-0.257 $\mu g/m^3$ was found in rural and urban communities sampled by the National Air Sampling Network in 1966 (NRC, 1977). "Fractional" airborne concentrations have been found near one copper smelter with occasional weekly averages of 1-2 $\mu g/m^3$. The validity of these data has been questioned because of possible contamination of air samples by the operation of conventional high-volume sampling equipment. Ambient concentrations, therefore, may be lower than reported (NRC, 1977).

B. ENVIRONMENTAL FATE

1. Overview

a. Methodology

In this section, the environmental fate is considered for copper released to the environment as a result of human activities. For each release of significant quantities to air, water, or land, the form of the copper in the discharge is identified, and the environmental pathway is described. Biological pathways are considered separately from physicochemical and bulk transport pathways. A general overview of the environmental chemistry of copper produced by Versar (1979a) has been used as the basis for formulating judgments concerning the direction and rate of transport of copper in any ecosystem. Other studies available in the literature support the observations noted and are discussed within.

b. Major Environmental Pathways

The major pathways of physical transport are designated in Figure 6. The rates at which the metal is transported are described in terms of the relative speed at which the transport occurs.

Separate pathways for atmospheric releases (Pathway 1) are shown for point source and dispersive emissions. Combustion processes, such as incineration, smelting and coal combustion contribute to highly localized pollution (1a); dispersive (non-point) sources such as corrosion of copper from chromeplated objects contribute to the concentration of copper found in urban runoff (1b). Pathway 2 follows the flow of copper originating from solid waste disposal dumps and mine tailings. As environmental controls restrain further discharges to air and water, the quantity of copper disposed of upon land surfaces and following this pathway can be expected to increase. Copper discharged with industrial process effluents into local surface waters or (POTW's) follows Pathway 3. The fate of copper in POTW's is described in Pathway 4. Deliberate releases of copper as in agricultural uses and as in algicide, are covered in Pathway 5.

Figure 7 gives a general overview of all major environmental pathways of anthropogenic copper. The figure also indicates the relative contributions of the copper industry and all other human activities to the major environmental pathways. The major impact on the land compartment (mostly at specific disposal sites) and the underlying groundwaters is to be noted. The migration of groundwaters containing copper to nearby surface waters has not been shown in this figure since (1) the process is very slow, and (2) the magnitude of the copper transported via this pathway is not well documented. Also not represented here is the high concentration of copper in sediments with respect to the overlying water and in soils subject to contamination by airborne copper.

c. Important Fate Processes

Copper is concentrated in the sediments in aerobic waters, sorbed primarily in hydrous iron and manganese oxides. Copper also sorbs to clays and organic material. Copper transported in the water column is in association with the dissolved or suspended solids. The primary complexing speciies are the organic agents such as humic acid; the aqueous carbonate and hydroxide are the predominant inorganic dissolved species. In anaerobic waters, the solubility of copper decreases; copper will exist in the reduced phase as metallic copper or cuprous oxide, or precipitate as copper sulfide.

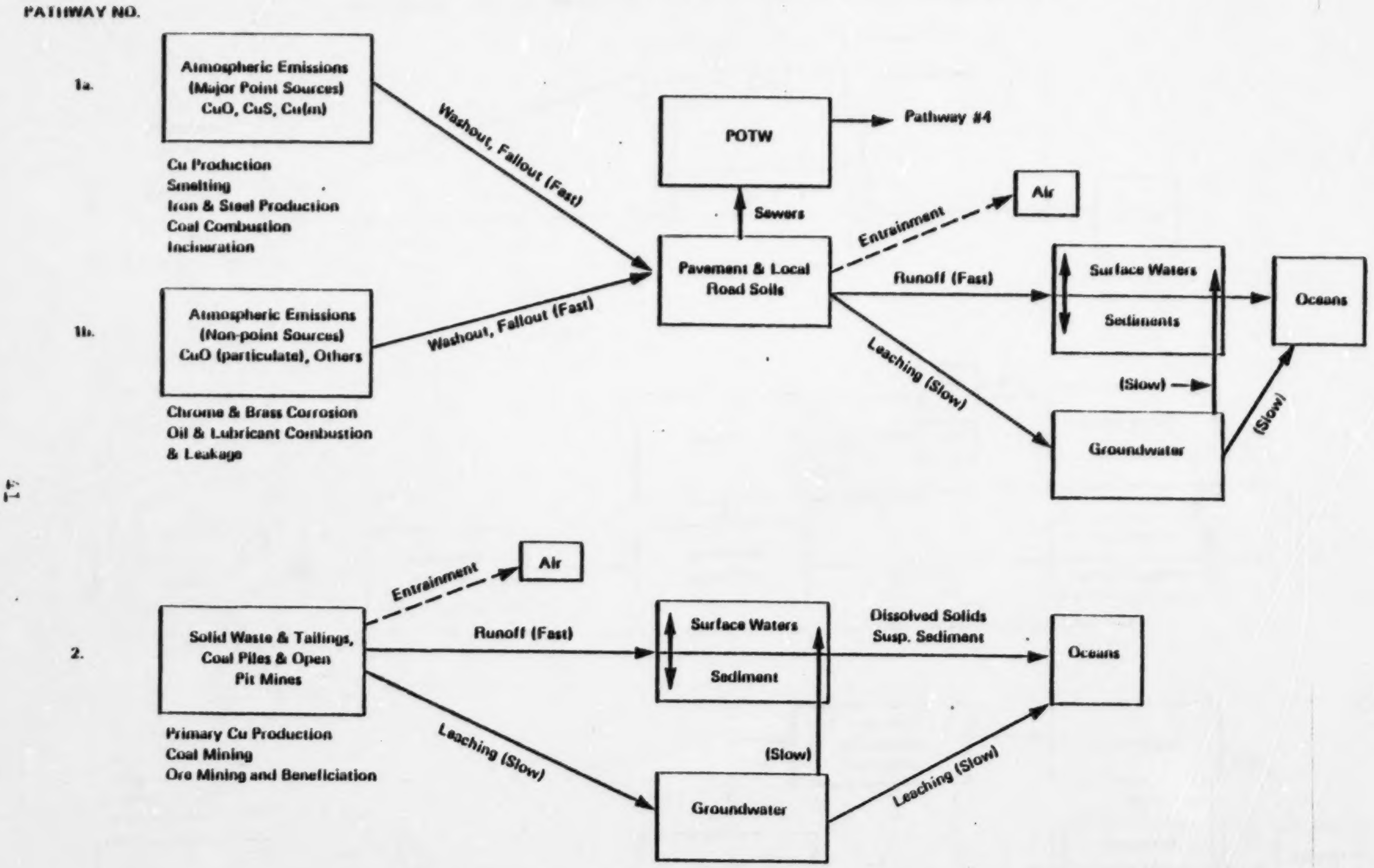

PATHWAY NO.
1a.
Atmospheric Emissions (Major Point Sources) CuO, CuS, Cu(m)
Cu Production
Smelting
Iron & Steel Production
Coal Combustion
Incineration
1b.
Atmospheric Emissions (Non-point Sources) CuO (particulate), Others
Chrome & Brass Corrosion
Oil & Lubricant Combustion & Leakage
Washout, Fallout (Fast)
Washout, Fallout (Fast)
Pavement & Local Road Soils
Sewers
POTW
Pathway #4
Entrainment
Air
Runoff (Fast)
Surface Waters
Sediments
Leaching (Slow)
(Slow)
Groundwater
(Slow)
Oceans
2.
Solid Waste & Tailings, Coal Piles & Open Pit Mines
Primary Cu Production
Coal Mining
Ore Mining and Beneficiation
Entrainment
Air
Runoff (Fast)
Surface Waters
Sediment
Dissolved Solids
Susp. Sediment
Oceans
Leaching (Slow)
(Slow)
Groundwater
Leaching (Slow)

FIGURE 6. MAJOR ENVIRONMENTAL PATHWAYS OF COPPER EMISSIONS

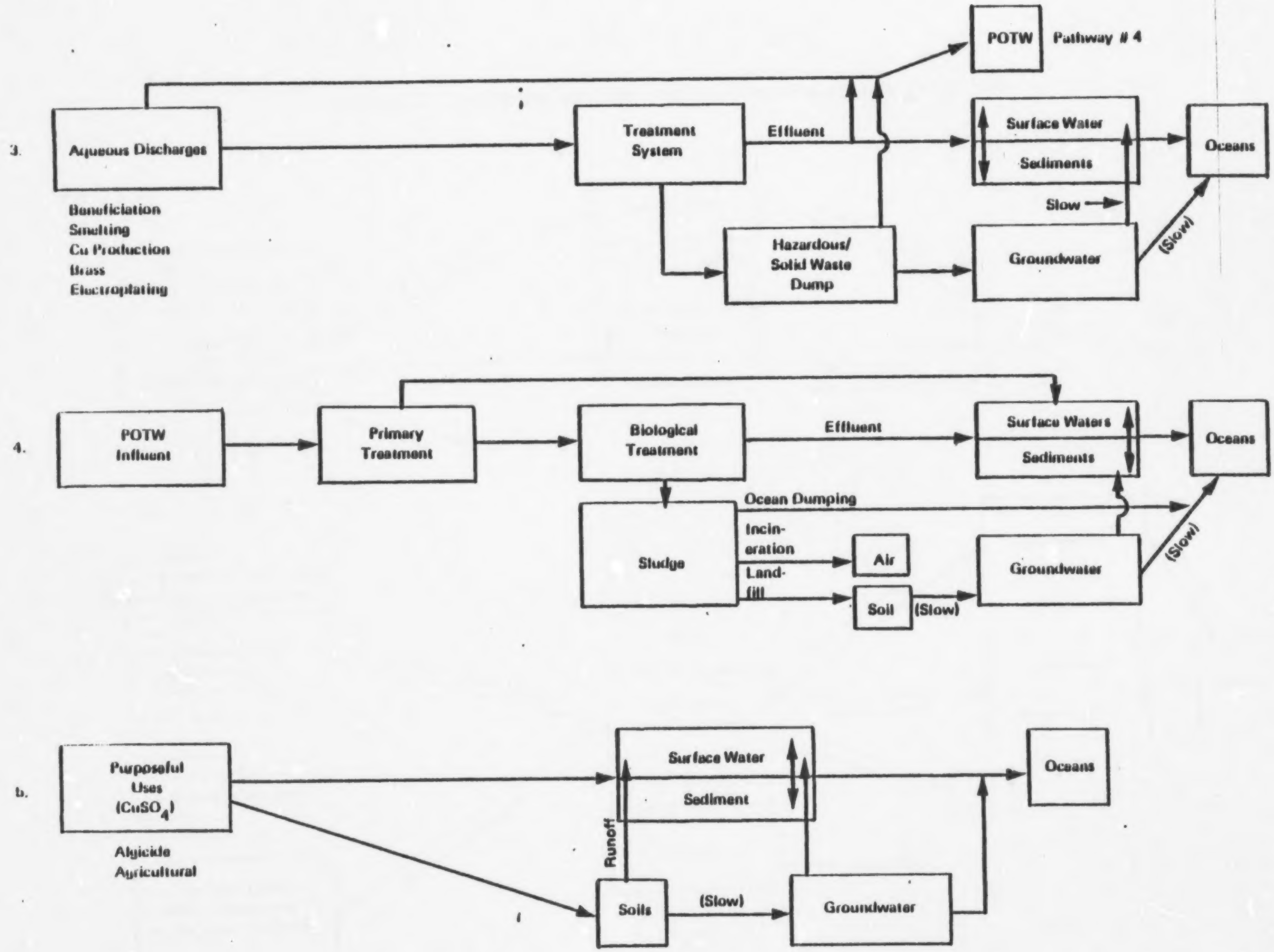
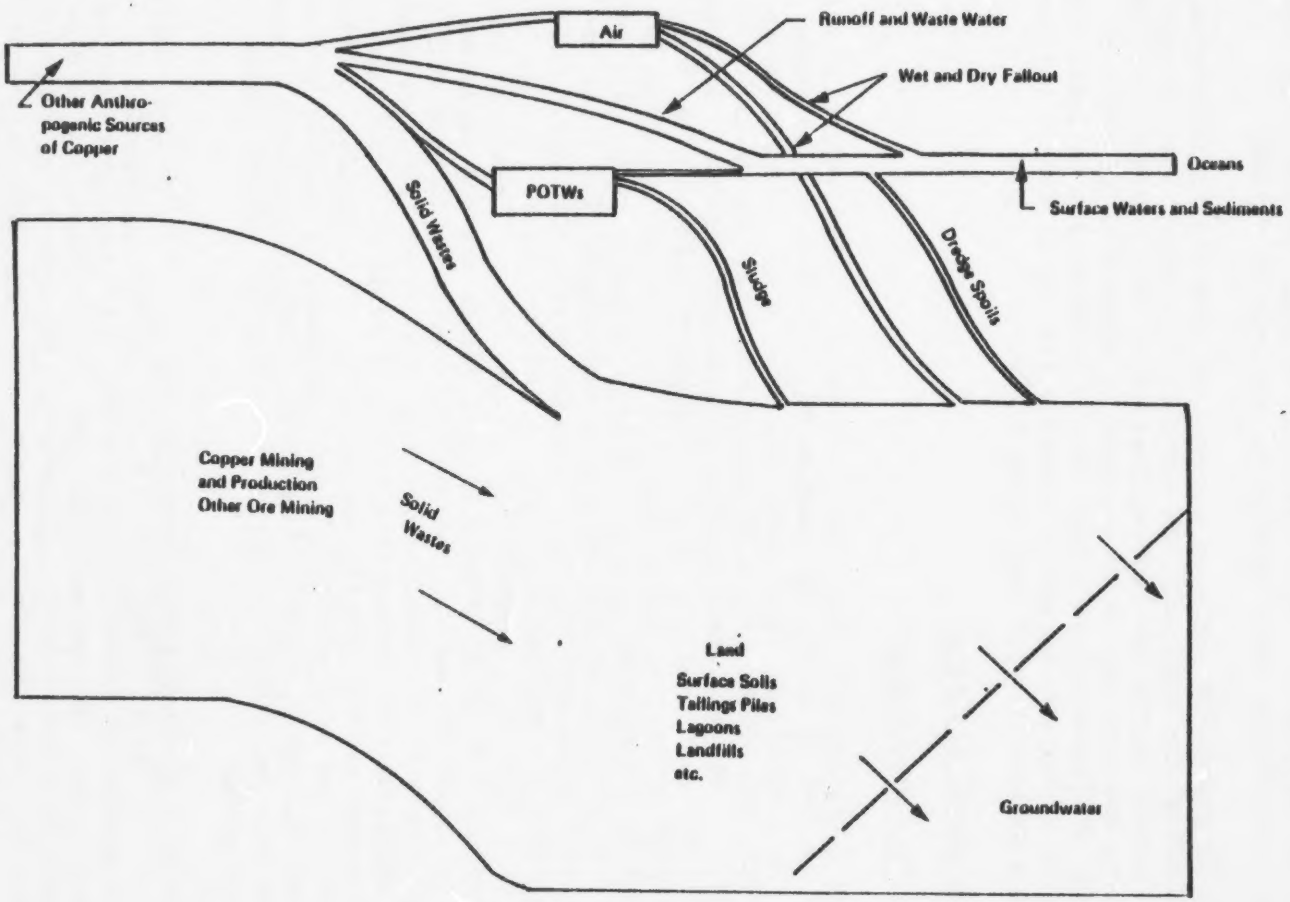

3.
Aqueous Discharges
Beneficiation
Smelting
Cu Production
Brass
Electroplating
Treatment System
Effluent
POTW
Pathway # 4
Surface Water
Sediments
Oceans
Slow
Hazardous/ Solid Waste Dump
Groundwater
(Slow)
4.
POTW Influent
Primary Treatment
Biological Treatment
Effluent
Surface Waters
Sediments
Oceans
Ocean Dumping
Sludge
Incin-eration
Land-fill
Air
Soil
(Slow)
Groundwater
(Slow)
b.
Purposeful Uses (CuSO4)
Algicide
Agricultural
Surface Water
Sediment
Runoff
Oceans
Soils
(Slow)
Groundwater

FIGURE 6. MAJOR ENVIRONMENTAL PATHWAYS OF COPPER RELEASES (Continued)


Air
Runoff and Waste Water
Wet and Dry Fallout
Other Anthro-
pogenic Sources
of Copper
POTWs
Oceans
Surface Waters and Sediments
Solid Wastes
Sludge
Dredge Spoils
Copper Mining
and Production
Other Ore Mining
Solid
Wastes
Land
Surface Soils
Tailings Piles
Lagoons
Landfills
etc.
Groundwater

Note: Quantities of copper moving in each pathway are roughly proportional to the thickness of each pathway shown. Slow movement from groundwaters to surface waters not shown.

FIGURE 7. SCHEMATIC DIAGRAM OF MAJOR PATHWAYS OF ANTHROPOGENIC COPPER RELEASED TO THE ENVIRONMENT IN THE U.S. (1979)

Atmospheric emissions of copper will consist mostly of copper sorbed to submicron particulate matter and the oxide of copper. A large percentage of the copper is expected to be short-lived in the atmosphere; dry fallout and washout of copper particulates will contribute to deposition upon local soils, urban pavements, and surface waters.

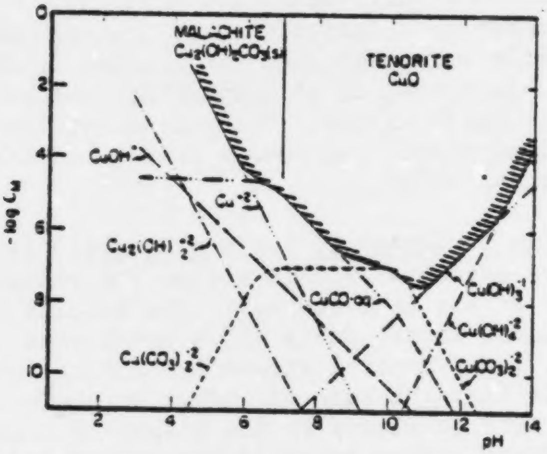
Copper is present in soils as a result of atmospheric deposition, solid waste and sludge disposal, and agricultural uses. Most of this copper will remain in the top few centimeters of soil, sorbed to organic matter, clays, and iron and manganese oxides, above a pH of about 5. The potential for translocation of copper to the groundwaters is small but can be an area of concern in sandy, porous sites, or in low pH environments, with a correspondingly high water table.

2. Physicochemical Pathways

a. General Fate Discussion

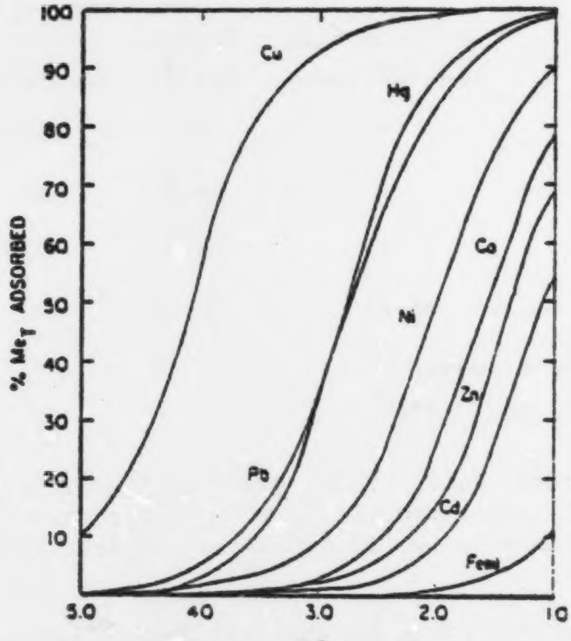
Aqueous Complexation: The concentration of soluble copper in water is directly related to parameters such as pH, the oxidizing potential of the water, the presence of other competing ions (e.g., calcium, magnesium and iron), the concentration of precipitating agents (e.g., OH^-, $S^=$, $PO_4^{\equiv}$, $CO_3^=$), and the concentration of complexing agents. Generally, at low pH values and in waters of low alkalinity copper will be more soluble; at high pH levels, and in highly alkaline waters, copper is usually found in a complexed form with organic ligands, carbonates and hydroxides. In natural, aerated waters cuprous copper (Cu(I)) is unstable, and will immediately oxidize to cupric copper (Cu(II)). Chloride, nitrate and sulfate complexes are highly soluble in water: 70.6 g, 138-244 g, and 14.3 g/100 H_2O, respectively (Weast, 1972). Insoluble forms of copper typically found in aerated natural waters are the oxide and hydroxide; in anaerobic waters, the insoluble sulfide, cuprous oxide, and metallic copper will predominate. Stumm and Morgan (1974) determined the copper complexes that predominate over a pH range of 0 to 14 in equilibrium with copper crystalline solids: malachite ($Cu_2(OH)_2CO_3$), azurite ($Cu_3(OH)_2(CO_3)_2$) and tenorite (CuO) The predominating soluble species above pH 7 are $CuCO_3(aq)$, $Cu(CO_3)_2^{=}$ and hydroxy copper complexes; below this pH, the free ion exists. Figure 8 indicates how complex copper chemistry may become.

Adsorption to Sediments and Suspended Solids: The computer program used by Vuceta and Morgan (1978) to calculate equilibrium species of heavy metals between pH 6.2-8.0 in the presence of naturally occurring inorganic and organic liquids indicates that copper solubility is dictated by the available colloidal surface area, represented in their calculations as SiO_2. When complexing agents (i.e., inorganic and organic ligands) are present in low concentration, sorption of Fe, Mn and Si oxides controls copper solubility. Figure 9 illustrates the ease with which copper is adsorbed compared with other divalent metals. The major aqueous species in solution would be Cu-OH and Cu-CO_3 complexes. Another



Reference: Stumm and Morgan (1970).

FIGURE 8. SOLUBILITY DIAGRAM OF Cu(II) IN EQUILIBRIUM WITH MALACHITE, AZURITE, AND TENORITE FROM pH 0–14



Reference: Vuceta and Morgan (1978).

FIGURE 9. ADSORPTION OF HEAVY METALS IN OXIDIZING FRESH WATERS (pH=7, pE=12, $pCO_2=10^{-3.5}$ atm., pCt—4.16) AS A FUNCTION OF SURFACE AREA OF SiO_2 IN ha/L. pS=—log (SiO_2) ha/L

study determined that humic acids are significant complexing agents for copper, and enhance metal adsorption to iron and manganese oxides by laying a thin film over suspended particulate matter (Davis and Leckie, 1978). As the concentration of complexing species increases (i.e., $CO_3^{=}$, OH^-, humic acid) partial or total desorption of copper may occur, with the dissolved copper complexing primarily with organic liquids (Vuceta and Morgan, 1978).

Distribution of Copper in Surface Waters: Perhac (1974) investigated the distribution of copper within stream bed sediments and the water column of three rivers in Tennessee. The results obtained are summarized in Table 10. These rivers drain (1) a rural area containing visible zinc mineralization, (2) a control stream and (3) an industrial river. The results indicate that the bulk of copper in the water column is transported through surface waters in the dissolved phase in these examples, although the highest concentrations exist in the particulate fractions. These data show a higher copper concentration in the colloidal particulates than in the coarse particulates, which agrees with other data showing an inverse correlation between copper concentration and sediment grain size.

TABLE 10. AVERAGE DISTRIBUTION OF COPPER IN THREE RIVER WATERS

	Particle Size (µm)	% Total Solids	Average Copper Concentration (mg/kg)	% Total Copper
Water	--	--	0.02	--
Dissolved Solids[1]		94.5	129	92.3
Colloids	<0.15	5.3	2454	1.3
Coarse Particulate	>0.15	0.11	1729	6.3

[1] Brought to dryness.

Source: Perhac (1974)

In contrast, Stiff (1971) reported that 12-57% of the total copper was present in the dissolved form in British rivers. Unfortunately, insufficient information is available to generalize from these conflicting results.

Another work determined the correlation between sediment and heavy metals by studying a river during periods of high discharge, at which time, deposited sediments are resuspended and transported downstream (Delfino, 1977). Although the correlation coefficient (r) between copper concentration and flow of total suspended solids was not very significant (about 0.5), the correlation of Cu with Fe was 0.94, and with Mn, 0.92. Since both Fe and Mn were primarily associated with suspended sediment (90%), the author concluded that copper must also be distributed in a similar manner, although measurements were not made to confirm this.

TABLE 11 COPPER CONCENTRATIONS AS A FUNCTION OF WATER HARDNESS AND URBANIZATION--TRIBUTARIES OF LAKE CAYUGA, N.Y.

Water Hardness/ Urbanization	Particulate Cu (mg/L)	Soluble Cu (mg/L)	Ratio of Particulate to Soluble Cu	Average Alkalinity (mg/L)
Hard Waters (n = 6)[1]	1.8	0.49	3.7	154
Soft Waters (n = 6)	2.6	0.86	3.0	90
Urban Streams (n = 4)	3.1	1.02	3.0	88
Rural Streams (n = 8)	1.7	0.50	3.4	139
Hard, Rural Streams (n = 6)	1.7	0.49	3.5	154
Soft, Rural Streams (n = 2)	1.55	0.53	2.9	94

---

[1] n = number of sites for which data were available.

Source: Kubota *et al.* (1974)

Reproduced from best available copy.

Kubota *et al*. (1974) reviewed the concentrations of trace metals associated with geochemical and soil weathering on twelve tributaries draining into Lake Cayuga, New York. Four of the streams also receive some anthropogenic contributions from urbanized areas. Table 11 summarizes the concentration of soluble and particulate copper as a function of alkalinity and urbanization. The pH was consistently between 8.1 and 8.3 and temperature between 10°C and 13°C.

The data in this table indicate that the concentrations of both soluble and particulate forms in hard water and in soft water rural streams do not differ significantly. The authors did not draw any parallels between copper concentration and alkalinity other than noting that high levels of hardness corresponded to high alkalinity values. Copper concentrations in the tributaries draining Ithaca, New York, were about two times those of rural streams, regardless of water hardness, or alkalinity.

Copper in the bottom sediments of the streams studied by Perhac (1974) associated with carbonates and iron oxides with minor amounts sorbed to organic matter, clays and perhaps sulfides. The form of copper in the sediments is not readily exchangeable or soluble in natural, alkaline waters, and would not be likely to contribute to biotic uptake. Table 12 summarizes the data pertaining to the stream water just after it passes over the mineralized area. It appears that the concentration of copper in the water column is not significantly affected by local fluxes in the sediment composition.

TABLE 12.. COPPER CONCENTRATION IN WATER AND SEDIMENTS AFTER EXPOSURE TO ZINC OUTCROP

	Copper Concentration	
Sample Site	Bottom Sediment mg/kg	Water µg/L
Mineralized Outcrop (carbonate rocks)	10	22
1 km downstream (carbonate rocks)	26	18
1.5 km downstream (clay strata)	25	21

Source: Perhac (1974)

The suspended particulates in the water column were found to concentrate copper more than the bottom sediments. This is due to the reduced surface area (and subsequent loss of sorption sites) of the sediments resulting from particulate flocculation prior to settling.

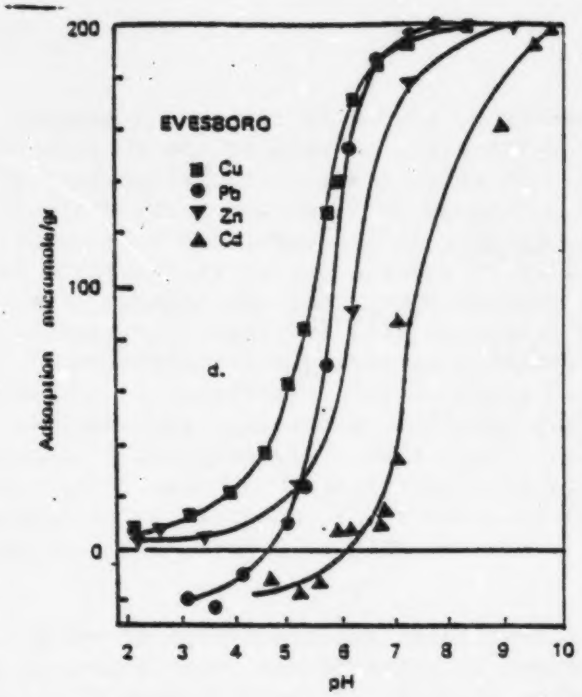
Soils: The behavior of copper in soils is dependent upon the adsorptive properties of the soil, as well as the pH and redox potential of the soil solution. In aerobic soils, the solubility of copper is controlled by CuO at a soil pH of 5 and carbonate and sulfur concentrations at 10^{-3}M (Huang et al., 1977); under the same conditions, CuS will control the availability of soluble copper in anaerobic soils. Copper is easily sorbed; it exceeds zinc, lead and cadmium in adsorbing potential. Adsorption of copper as well as other heavy metals onto hydrous oxides and soil particulates is strongly dependent on pH, as illustrated in Figure 10. At a pH range of 5-6, adsorption is the principal means of removing copper from solution; above this pH, chemical precipitation becomes more dominant. Below a pH of 5, sorption of copper becomes insignificant. Figure 10 illustrates this trend. The presence of organic ligands, such as humic acids, enhances metal adsorption at low pH values. Humic acid was the most effective ligand in this respect, out of five tested.

Summary: The concentration and speciation of soluble copper in the water column is dependent upon the pH and redox potential of the water and nature of complexing ligands. In natural aerated waters, Cu(II) complexes with organic ligands, carbonates, and hydroxides. In reduced environments, copper will be present as cuprous oxide, metallic copper and CuS.

Copper adsorbs to iron and manganese oxides, clays, and organic matter in the sediments. Its tendency to adsorb exceeds that of other divalent metals. Suspended solids concentrate copper; at times this concentration exceeds that of the sediments due to a greater number of adsorption sites on suspended sediment. However, the amount of copper in suspended sediments is usually small compared with the amount of copper found in the sediment.

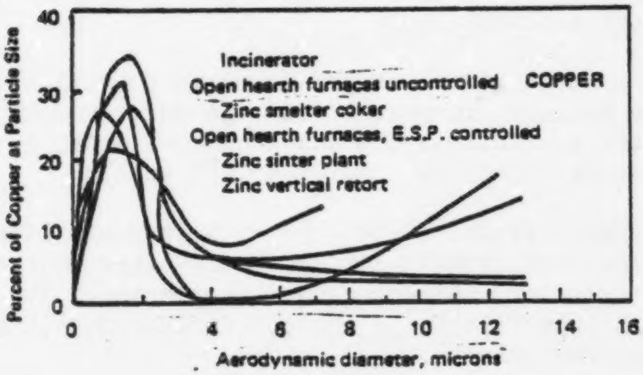
In conclusion, most of the copper found in natural waters, is partitioned with the sediment component. In the water column, concentrations of copper are greatest in the suspended sediment, but the greatest mass of copper may be found with the dissolved solids.

In soils, copper adsorbs above a pH of 5; organic liquids, especially humic acid, enhance this trend. Compared with other metals, copper demonstrates the greatest tendency toward adsorption. In acid environments, copper will be available in the soil solution, although to less of an extent than other metals.



Reference: Huang et al.(1977)

FIGURE 10. ADSORPTION OF HEAVY METALS ON SOIL MINERALS AND OXIDES

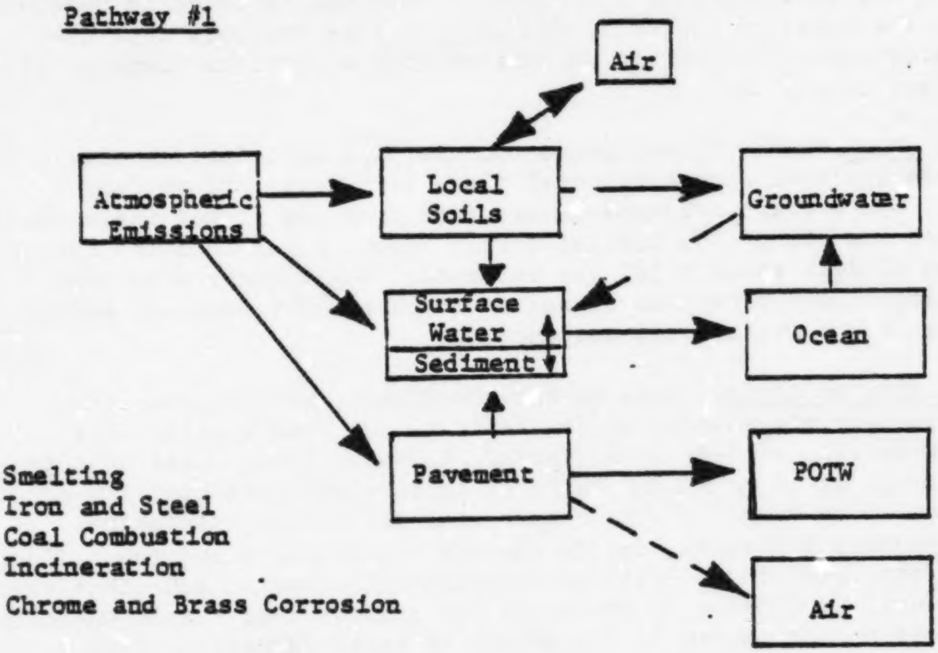


Reference: Jacko and Neuendorf (1977)

FIGURE 11. AERODYNAMIC PARTICLE SIZE DISTRIBUTION OF COPPER IN INDUSTRIAL STACK EFFLUENT

b. Atmospheric Transport

Pathway #1



Sources: Pathway #1 describes the fate of copper as a result of stationary source air emission from smelting, iron and steel coal combustion and incineration. In addition, area sources such as chrome and brass corrosion have been included in this pathway. Although these releases may not be strictly atmospheric, their pathway to pavement and local soils is similar. The forms of copper released due to thermal processes are the oxide, (CuO), elemental copper, as the vapor, and absorbed on particulates; copper sulfide, as the dust, is the result of entrainment from coal pits.

Once copper has been released into the atmosphere, its residence time and distance travelled are dependent upon its particle size, as well as meteorological factors. Copper from combustion sources tends to associate with sub-micron particulate matter due to selective adsorption of the copper vapor upon particulates with a large surface area to volume ratio (Jacko and Nueundorf, 1977). Jacko et al. (1975) investigated the metal distribution upon particulates emanating from municipal and industrial incinerators. They found that the concentration of copper adsorbed to particulates increased twenty times as the diameter of the particle decreased from 4.6 µm to 0.6 µm. The work of Coles et al. (1979) supports this trend. Copper was partitioned amongst fly ash particulates in the following manner: 56 mg/kg on 18.5 µm fraction, 89 mg/kg on 6.0 µm, 107 mg/kg on 3.7 µm and 137 mg/kg on 2.4µ m fraction. Figure 11 illustrates the distribution of copper adsorbed to particulates resulting from a variety of industrial stacks (Jacko and Neuendorf, 1977). The zinc vertical retort, zinc smelter, and open hearth furnaces had no air pollution control devices, the zinc sinter plant, and indicated open hearth furnaces were controlled by electrostatic precipitators; the incinerator was equipped with a scrubber. Although no trend is observable concerning the types of controls, the diagram does indicate that the largest percentage of copper is associated with a particle diameter of somewhat less than 2 µm.

Jacko et al.(1975) investigated the cleaning efficiencies of incinerators equipped with horizontal plate scrubbers, and venturi scrubbers. The average atmospheric emission from the former incinerator (for refuse) was 38% of the initial copper input, while from the latter (for sewage sludge) about 0.10% was released. The authors concluded that the large discrepancy was caused by scrubber efficiencies, not by differences in the incinerated contents.

Deposition on Soils: Once in the atmosphere, particulates are deposited quickly via rainout or dry fallout, and this results in a mean residence time of 7-30 days (Versar, 1979b). Though most of this deposition will occur over land surfaces in the immediate vicinity of the emission source, some of the copper will clearly be transported over much greater distances due to the small particle size; the fallout will vary from location to location depending on climatic and other factors. The trace metal enrichment in the soils and grasses near a lead smelting complex gives an indication of the extent of metal deposition from aerial sources (Ragaini et al., 1977). The average concentration of copper in the top 2 cm of soil was 278 (± 108) mg/kg within 2 miles of the smelter. The background concentration, measured between 3.3 and 7.8 miles from the smelter, did not exceed 185 mg/kg. For grasses, the copper concentration ranged from 38 mg/kg to 110 mg/kg in the contaminated sites, and from 21 mg/kg to 26 mg/kg in the background area.

Versar (1979a) states that copper is tightly bound to hydrous iron and manganese oxides, and clays, making these components of the soil the major control mechanisms for copper mobilization. The work of Huang et al. (1977) supports this statement, which concludes that even at pH values as low as 5, copper does not readily desorb off soil particles. (See previous discussion of general fate in soils--IV-B-1. c.)

According to Versar (1979b), the deposition of copper upon the soil surface allows for the entrainment of soil particles containing copper back into the atmosphere. This cycle is dependent on, among other parameters, groundcover and soil moisture, and will continue indefinitely. Once the copper is airborne, the same type of physical phenomena discussed previously will apply. Surface runoff of soil particulates will also result in the introduction of copper into surface waters and sediments. Bioaccumulation of deposited copper will be another pathway, among both terrestrial and aquatic organisms. However, the bulk of the copper that is deposited upon soil surfaces will remain bound up in the soil compartment.

Fallout in Urban Areas: Deposition of particulates in urban areas is due to combustion plants within the city, such as incinerators and coal-fired power plants, and corrosion of products containing copper, such as chrome and brass. Kleinman *et al*. (1977) determined the flux of atmospheric fallout over New York City by placing dust collectors on three rooftops in Manhattan. The data for copper indicated that the element remains at a relatively low constant baseline, with sporadic large spikes of concentration, as indicated in Figure 12. The range in the average deposition rates for copper was 800-1,700 ng/cm^2/month. The authors then determined the concentration of copper in street runoff entering the New York Harbor resulting from atmospheric deposition:

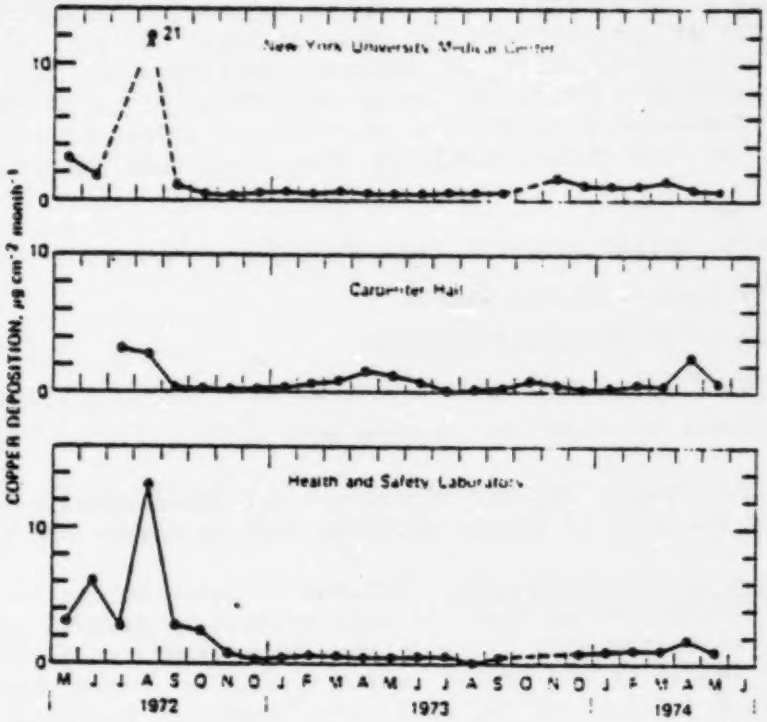
Atmospheric copper dustfall (ng/cm^2/month)	750
Estimated [Cu] in runoff (mg/L)	0.06
Discharge of Cu in runoff (kg/day)	210
Discharge of Cu - other sources (kg/day)	1,100
% Contributed by runoff to surface waters	16%

According to this study, fallout of copper over urban areas contributes appreciably to the flux of copper entering surface waters via runoff.

Deposition on Surface Waters: Fallout of heavy metals in the southern California coastal zone has been studied by Bruland *et al*. (1974). They estimated that anthropogenic sources of copper contribute 1.3 μg/cm^2/yr (= 108 ng/cm^2/month) to the sediments, while natural processes account for 1.6 μg/cm^2/yr (133 ng/cm^2/month). The flux of copper due to rainfall had been reported in a previous study as 0.5 μg/cm^2/yr (42 ng/cm^2/month). In order to determine the relative contribution of washout to the anthropogenic fluxes observed in the bay, they estimated that over a 12,000 km^2 area, 567 tons Cu/yr was due to contributions from wastewaters, 18 tons/yr from stormwater runoff, and 60 tons/yr from washout. The flux of copper from anthropogenic sources to the sediments amounts to 160 tons/yr. Therefore, both the stormwater runoff and washout contribute significantly to the anthropogenic fluxes observed in the bay (12%).

The air-water interface, or surface microlayer, is frequently studied due to its ability to concentrate pollutants. In southern Lake Michigan, the surface particulate microlayer contained 190 μg Cu/g, while the bulk water particulates contained 30 μg/g (Elzerman *et al*. 1972). Entrainment of aerosols containing copper from the air-water interface is a probable means of copper transport.

Peyton and McIntosh (1974) compared the sediments of a borrow pit near industrialized Gary, Indiana, with those in a rural control pond. In the top 5 cm of sediments, the borrow pit contained 52.1 mg/kg Cu, while the rural pond contained 10.0 mg/kg. The metals entering the system



Reference: Kleinman et al. (1977).

FIGURE 12. MONTHLY DEPOSITION OF ATMOSPHERIC COPPER IN NEW YORK CITY

through the air were associated with a maximum particle size of 10 μm. The concentration of copper in one core typified the distribution:

Sediment Size Range (μm)	[Cu] mg/kg
750	13
50-20	60
20-10	80
10-2	66
< 2	89

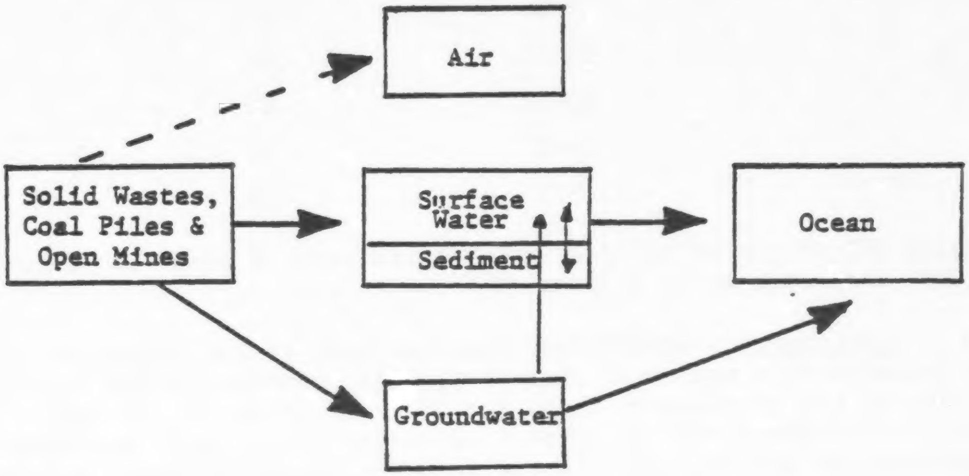
About 50% of copper resides with particulates of less than 10-μm diameter that apparently originated from the air.

Groundwater: Groundwater contamination by the copper ion will be a function of a number of parameters, the two most obvious being the depth to the groundwater table and the composition of the soil. However, as demonstrated by copper's affinity toward soil particulates, groundwater contamination is not probable except in sandy, porous soils. Most of the particulate copper that is deposited exists as the oxide. Initial copper mobility will depend upon the solubility of the copper compounds deposited. Copper oxide is highly insoluble in water, as is copper sulfide. Copper sorbed to particulates will not readily desorb.

Summary: Copper enters the atmosphere primarily from point-source combustion processes and to a lesser extent from dust from coal piles and tailings and aerosol entrainment and corrosion. Copper is sorbed preferentially to submicron particulates, whose residence time in the atmosphere is subject to meteorological conditions such as washout and fallout. Localized pollution of soils, pavements and surface waters results from point source emissions. The percentage of copper from aerial deposition contributing to the concentrations found in urban runoff and washout has been found to be significant.

c. Solid Wastes

Pathway #2



Sources of Solid Wastes, Tailings and Coal Piles, etc.: Most of these materials arise from mineral ore processing, and coal mining. The solid wastes result from the overburden of surface mining and the low-grade portions of mineral ore deposits. The tailings, which contain highly concentrated minerals, are produced as a final waste product of mineral concentrating operations (Martin and Mills, 1976). Other wastes may be derived from a variety of other industrial processes or from municipal refuse.

Since 1845, the production of copper has contributed 5780 million MT of tailings, and 14450 million MT of combined tailings and waste (Martin and Mills, 1976). Disposal of these wastes in the 19th and 20th centuries was without regard to environmental considerations, and thus, erosion and weathering contributed to adverse ecological impacts. Currently, tailings are left to settle in lagoons, after treatment with lime to raise the pH and precipitate heavy metals.

The nature of the solid wastes and tailings depends upon the nature of the ore. Copper ores are numerous. A few representative ores are azurite ($2\ CuCO_3.CU(OH)_2$), cuprite (Cu_2O), bornite (Cu_5FeS_4), chalcocite (Cu_2S), and chalcopyrite ($CuFeS_2$); this last one being the most abundant (Versar, 1979a). The host rocks for these minerals are granite (10 mg/kg Cu), sandstone (30 mg/kg Cu), limestone (4 mg/kg Cu), and basalt (100 mg/kg Cu). Coal piles and solid wastes from coal cleaning processes may also be sources of copper for the pathway being considered. One survey of 101 samples of U.S. coal showed a mean copper concentration of 15 mg/kg, with a range of 5 mg/kg to 61 mg/kg and a standard deviation of 8 mg/kg (Mezey *et al*., 1976). Levels of copper have been shown to have a positive correlation with pyrite (FeS_2)

in coal, and copper often occurs in conjunction with nickel. Copper is mostly concentrated in the mineral matter of coal, but can be associated with organic matter. The association of copper with pyrite implies that copper may be concentrated in the solid wastes from any coal cleaning operation designed to remove pyritic sulfur and/or other inorganic mineral matter from coal.

Acid Mine Drainage: Tailings and solid waste from mineral mining aid in the formation of mineralized acid discharge. This is caused by the exposure of fine particulates to air, upon which the oxidation of metal sulfides results in the formation of sulfuric acid. The impact of acid mine drainage to local surface waters is largely dependent upon the alkalinity, or buffering capacity, of the waters upstream and downstream of the point of discharge. Pyrite, with which copper associates, is easily oxided to $Fe(OH)_3$, producing acidic waters as a consequence of the reaction. Igneous rocks, which host pyrite, are low in calciferous material and, therefore, the water that passes over the gangue has little opportunity to dissolve carbonates and become a buffered solution. For these reasons, a large potential exists for adverse impacts to the local waters of a mined region.

Fate Processes in Streams: Figures 13 - 15 summarize observations for a stream that receives acid mine drainage (AMD) (Martin and Mills, 1976). The mine occurs at kilometer 35 and the confluence of two streams occurs at 0 kilometers. The pH and bicarbonate concentration in stream waters drop immediately. At the same time, the concentration of dissolved copper increases dramatically. These figures also give an indication of how the stream's recovery is a function of distance from the source.

Precipitation, adsorption and dilution reduce the concentration of copper in the water column (Martin and Mills, 1976). A literature review performed by Versar (1979a) concludes that sorption is the dominant process affecting the reduction of copper in surface waters. Sorption upon hydrous iron and manganese oxides, clays and organic matter results in enriched sediments and suspended solids so that Cu concentrations in these fractions are in the mg/kg range, while the water column exhibits concentrations of copper in the µg/L range. Holcombe (1977) found that copper draining a mined area sorbed preferentially to manganese oxides rather than to iron oxides. Iron oxides exhibit a positive surface charge at low pH values, repelling the copper ions, while the opposite is true of manganese oxides.

Groundwater Contamination: Contamination of groundwaters by metals leaching through tailing piles has been cited by Martin and Mills (1976). Leaching of acid mine drainage is a function of the tailing pile porosity. Tailings from years ago were higher in porosity, and this allows more active leaching to occur. One may surmise that the acid nature of the leachate and porosity of the piles allow greater translocation of copper than would be found under controlled landfill conditions.

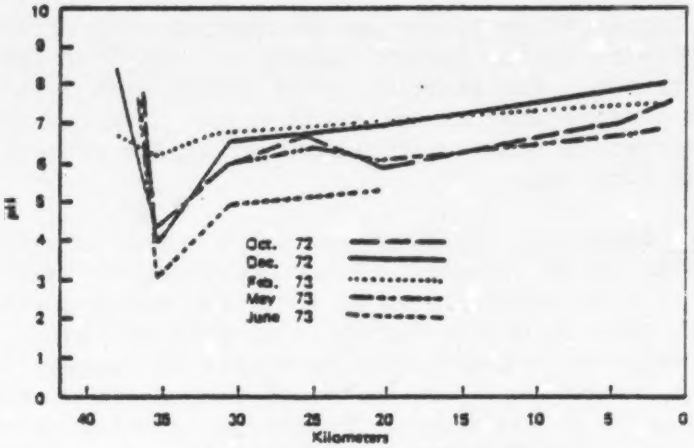


FIGURE 13. THE pH IN KERBER CREEK

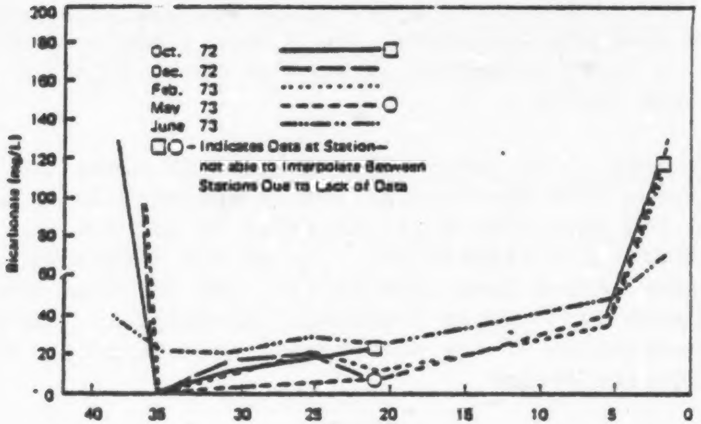
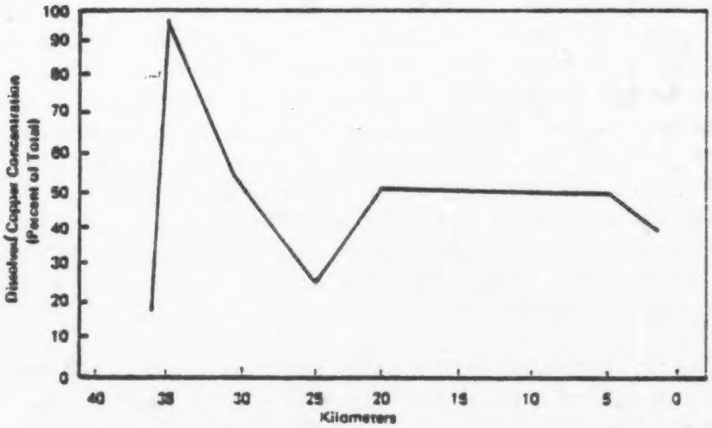


FIGURE 14. BICARBONATE CONCENTRATIONS IN KERBER CREEK



Reference: Martin and Mills (1978).

FIGURE 15. DISSOLVED COPPER CONCENTRATION IN KERBER CREEK

Disposal of municipal solid wastes and subsequent leaching of metal were studied at two sites (Roulier, 1975). At the first site, leachate was collected from 1390 kg of municipal refuse under anaerobic conditions. The concentration of copper was below the detection limit of 0.05 mg/L. In order to simulate contaminant migration, metal salts were brought into solution (100 mg/L) and slowly passed through soil columns packed with sand and clay minerals. The soil columns were then leached with water in order to distinguish the more mobile metals, and subsequently, with 0.1 N HCl to identify the tightly-bound metals. Copper fell into the category of "least generally mobile." At the second site, soil columns were packed with whole soils (organic and inorganic components) and the initial metal concentrations and flow rates were higher. Even under these conditions, copper was almost completely attenuated. Data from other landfills show copper concentrations in leachate ranging from 0.01 mg/L to 2.0 mg/L, with 0.04 mg/L being a typical value; copper was considered to be a significant pollutant in leachate since the concentrations found were significantly higher than those found in nearby (unaffected) groundwaters (U.S. EPA, 1977b). Another study of 12 landfills ranging in age from 0.25 years to 16 years showed a mean copper concentration in the leachate of 0.41 mg/L (range 0.1 - 1.0 mg/L range) (Chian and DeWalle, 1977); this is an order of magnitude greater than the results of the above study.

Analysis of leachate from a power plant ash pond revealed 12.2 mg/L particulate copper and 275 mg/L soluble copper (Theis and Richter, 1979). Within 100 m of the pond, copper was available as the ion and as copper sulfate. At a distance of 400 m from the pond, some of the copper was associated with hydrous iron and manganese oxides, while most precipitated as $Cu_2(OH)_2CO_3(s)$. However, fly ash also serves to attenuate the migration of heavy metals. One study found that about 4.7 ng of copper will sorb to 1 g of fly ash; the alkalinity and pH of the fly ash ponds promote the precipitation and deposition of copper in an insoluble form (Chu *et al*., 1978).

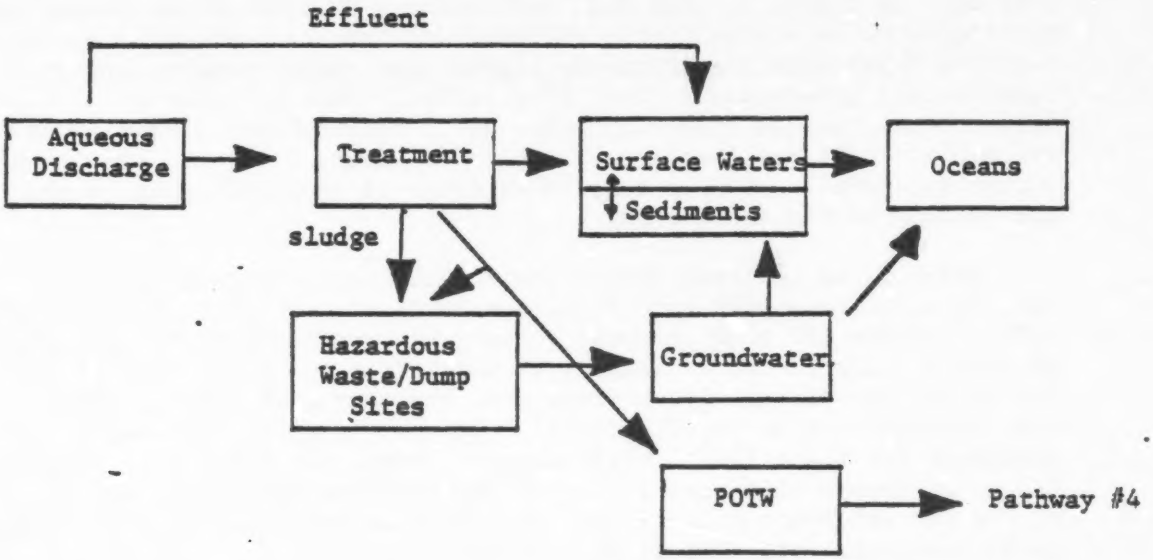
Ultimate Sinks: Lakes or oceans that are fed by streams or groundwater from mined areas and solid and hazardous waste sites may serve as the ultimate sink for copper. The effect of a polluted stream on a lake is a function of the volume of pollutants introduced to the lake and the natural buffering capacity of the lake. Martin and Mills (1976) suggest that the most notable effects of acid mine drainage will result at the mouth of the stream. It is likely that the stream drops its suspended load when its velocity is slowed upon entry into the lake.

Summary: Solid wastes, coal piles, and tailings are sources of copper disposed of on land. Copper disposed as a result of mining practices is subject to greater translocation in the environment due to the acid nature of the leachate. Surface streams draining mined areas experience localized spikes in copper concentration. The level quickly decreases as the stream recovers in pH and alkalinity values as a function of distance from the release. The major processes affecting the reduction in copper concentration are dilution, sorption and precipitation.

Studies of municipal waste landfills found that the copper concentration in leachate typically falls between 0.04 mg/L and 0.4 mg/L. Copper is quickly attenuated by the soil. No data was found regarding groundwater contamination. Such contamination is not likely to occur in a properly operated landfill. In old mined areas, acid mine drainage and porous tailings enhance the possibility of groundwater contamination.

d. Aqueous Industrial Discharge

Pathway #3


Effluent
Aqueous Discharge
Treatment
Surface Waters
Sediments
Oceans
sludge
Hazardous Waste/Dump Sites
Groundwater
POTW
Pathway #4

Sources and Treatment: Pathway #3 considers the fate of copper discharged with industrial wastewater effluents. The industries that discharge copper are numerous; the major ones are involved in copper wire production, electroplating, brass manufacture and scrap refining. Industrial effluents are discharged with or without treatment into natural waters or municipal wastewater treatment systems. Yost and Masarik (1977) have investigated the efficiency of "chemical-destruct" systems, of the sort employed by the metal finishing industries. Neutralization and precipitation of copper in a waste effluent originating from 90% steel and 10% brass were found to result in copper removal as summarized below:

Treatment	[Cu] mg/L	% Removed
CN system output	0.65	70%
Settling Tank Output	0.15	64%

The distribution of copper in the treated wastewater averaged 0.07 mg/L (28.5%) in the dissolved phase, and 0.41 mg/L (71.5%) in the suspended solid phase. These results suggest that copper discharged with treated wastewater effluents is most concentrated in the particulate phase.

Yost and Scarfi (1979) determined the factors affecting copper solubility in electroplating wastes. Their results indicated that at the pH normally used for alkaline precipitation (8.5-9.5), CuCn was more soluble than $CuSO_4$, and that as the initial Cu concentration increased, the solubility of CuCn increased; the solubility of $CuSO_4$ was not affected. This indicates that concentrating a CuCN waste prior to treatment will increase the amount of copper discharged. Their data also revealed that the concentration of soluble copper increased when CuCN was mixed with zinc and cadmium plating solutions and decreased with nickel plating solutions. These observations led the authors to suggest that effective copper treatment is realized by treating copper cyanide solutions separately from zinc and cadmium plating wastes, or in conjunction with a nickel plating solution.

The effluent of industrial waste treatment is discharged to municipal sewers or surface waters. The fate of copper, once it reaches a POTW, will be discussed separately in Pathway #4.

Distribution in Surface Waters: The distribution of copper discharged into surface waters from industrial plants has been studied by Mathis and Cummings (1973), who used the Illinois River as their environmental system. The river is known to receive both municipal and industrial waste discharges. When compared with non-industrial-use (rural) rivers, the average copper concentration in the sediments of the Illinois River (19 mg/kg) was found to be 2.5 times that of the rural rivers (7.7 mg/L). A study of trophic level concentrations revealed that the sediments and benthic feeders were the greatest accumulators of copper as revealed below:

Ecosystem Component	Average Copper Concentration (mg/kg)
Water Body	0.005
Carnivorous Fish	0.13
Omnivorous Fish	0.21
Clams	1.5
Tubificid Annelids	23
Sediments	19

A study of methods for treatment of copper wastes resulting from scale and corrosion products from boiler tubes showed that discharge of the effluent into a fly ash pond results in removal of copper both by precipitation (at pH greater than 10) and adsorption (Chu et al., 1978). Generally, about 4.7 μg of copper will be adsorbed onto each gram of fly ash, regardless of the pH level.

The behavior and distribution of copper discharged as an industrial waste into a marine environment has been investigated by Stoffers et al. (1977). The waste effluent studied was reponsible for adding approximately 200 lb Cu per day into Buzzards Bay. Analysis of the clay fraction (<2 μ) of sediment cores sampled in the Bay revealed the following:

Core Sample & Depth	[Cu](mg/kg) in Clay
A. Near discharge, 0-20 cm	3136
B. Midway, 0-10 cm	580
C. Edge of Bay, 0-5 cm	117
D. Background	20

Unfortunately, it is difficult to discern a definite trend in these data, since the core sampling depth was not held constant. It is interesting to note, however, that the copper concentration at the end of the Bay is three times the background level, suggesting that the estuary may act as a pollutant sink. The authors found that 39% of the copper resided with the insoluble mineral detritus (clays), 18% with the authigenic phase (minerals residing in sedimentary rock), and 42% with the organic fraction of the sediment. The work of Serne (1977) supports this distribution. He found that copper in the San Francisco Bay sediments is partitioned as follows:

	Copper	
Sediment Component	Average Concentration (mg/kg)	%
Interstitial water	0.2	0.16
Exchangeable phase	0.8	1.1
Carbonates, Mn Oxides	0.4	0.5
Organics, Sulfides	43	41.3
Iron Oxides	5	5
Clays	49.3	51.8
TOTAL	98.7	

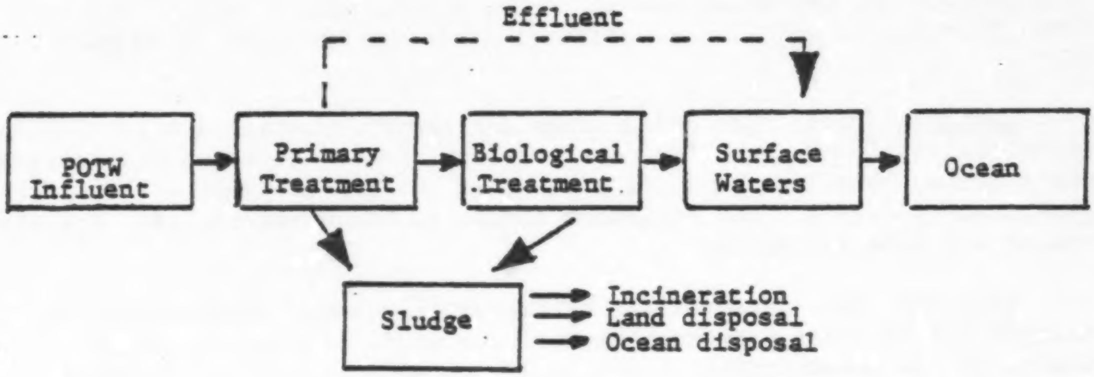
Sludge Disposal: The sludge generated by industrial effluent treatment is normally disposed of in a solid or hazardous waste dump or a settling pond. A properly designed hazardous waste dump should prevent further translocation of copper due to leaching. At some sites the leachate is collected and sent to a POTW (with or without further treatment). Groundwater contamination is possible in a poorly operated landfill or settling pond. The speed at which copper is translocated in this pathway is very slow, due to copper's affinity to soils. The fate of copper in solid waste disposal sites was reviewed in Pathway #2.

Ultimate Sinks: The major sinks for copper associated with treated industrial effluents are, in the short term, local waterways and hazardous waste dumps, settling ponds, or sites used for the disposal of sludge generated by POTW's. The long-term sinks, as discussed earlier, are the oceans and lake sediments.

Summary: The concentration of copper in aqueous industrial discharges may be lowered by treatment of the waste effluent prior to discharge, as demonstrated by the metal-finishing industry. Surface water sediments are the best indicators of anthropogenic inputs, as are the benthic organisms. Marine sediments also reflect these inputs, with copper distributed principally with the organic, sulfide and clay components of the sediments. Disposal of sludge generated by waste treatment in a properly-operated landfill should prevent further translocation of copper.

e. POTW

Pathway #4


Effluent
POTW Influent
Primary Treatment
Biological Treatment
Surface Waters
Ocean
Sludge
Incineration
Land disposal
Ocean disposal

Treatment Schemes: Pathway #4 describes the fate of copper in wastewaters that are introduced into a POTW. The inflow to the POTW may consist of combinations of industrial and commercial effluents, domestic wastes, and surface runoff. Though the nature of the influent into each POTW is quite varied, typical copper concentrations are about 0.01-1.97 mg/L* (Sverdrup and Parcel, 1977). Domestic wastes have been estimated to contribute about 50% of the copper as determined by averaging the data of the three cities used for the study of Davis and Jacknow (1975).

The degree to which copper is removed from the raw wastewaters, and thus the concentration of copper in the discharged wastewaters, depends on the type of treatment involved. One report provides a summary of data from 269 municipal treatment plants in the U.S. using various treatment methods (U.S. EPA, 1977a). The data for copper are summarized below.

---

*Activated sludge treatment processes are likely to be inhibited by influent copper concentrations above 1 mg/L (U.S. EPA, 1979a).

Type of Treatment	Effluent Data (Means) Removal of Cu (%)	 Cu Concentration (mg/L)
Primary	26	.19
Biological (all types)	26	.13
Activated sludge	57	.19
Trickling filter	54	.13
Biological with chemical addition	75	not available
Tertiary	73	not available

These data, as well as other sources, are described in Section III.

The notion of concentration-dependent removal efficiency for copper from POTW influents can be demonstrated from the data generated from an activated sludge treatment plant in Grand Rapids, Michigan (Biener and Bourma, 1978). In 1968, the metal platers and other industries were forced to pretreat their waste prior to discharge into the sewer. Before this requirement, 25% of 2.8 mg/L copper in the influent was removed in the municipal treatment plants; after pretreatment enforcement, 63% of 0.30 mg/L copper was removed. Figure 16 illustrates the reduction of copper concentrations in sewage at the Grand Rapids plant.

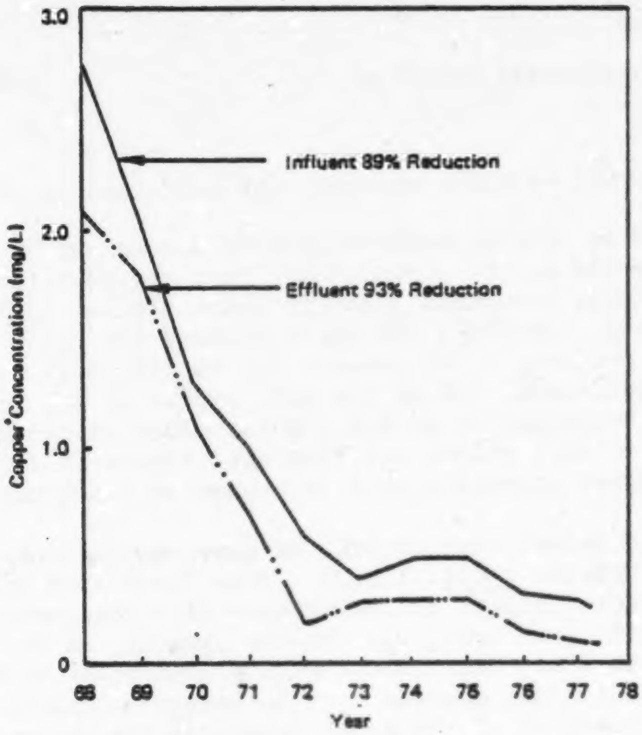
Support for enforcement of pretreatment regulations is indicated in the work of Mytelka et al. (1973). They found that high copper concentrations in the effluent following secondary treatment were due to influent concentrations too large for the capacity of the treatment system. When the waste was treated at the industrial site where it is generated, the municipal systems were not overstrained and were able to ensure proper treatment of the heavy metals in the waste.

Copper is partitioned into the sludge portion of the waste during treatment. A study of 205 sewage sludges showed copper levels of 84 mg/kg to 10,400 mg/kg, with 1210 mg/kg as the mean value and 850 mg/kg as the median (U.S. EPA, 1979). Industrial pretreatment of wastes destined for POTW's can significantly reduce the copper content of POTW sludges. The percentage of industrial contributions to these POTW's was not stated. However, it is known that all three cities sampled are highly industrialized. Three examples are given below (U.S. EPA, 1979a):

City	Copper Concentration (dry basis) in POTW Sludges Before Pretreatment (mg/kg)	 After Pretreatment (mg/kg)
Buffalo, NY	1,570	330[1]
Grand Rapids, MI	3,000	2,500
Muncie, IN	1,750	700

---

[1] Projected



Reference: Biener and Bourme (1978)

FIGURE 16. TOTAL COPPER IN SEWAGE AT GRAND RAPIDS, MICHIGAN BEFORE AND AFTER PRETREATMENT OF INDUSTRIAL DISCHARGES TO A POTW

Sommers et al. (1976) found that after 9 weeks of anaerobic digestion, a 2-L quantity of synthetic sludge containing ash and organic matter typical of municipal sludge, plus 96.1 mg $Cu(NO_3)_2 \cdot 3H_2O$, retained less than 0.2 mg/L (the detection limit) of water-soluble Cu. The air-dried sludge retained approximately 700 mg/kg Cu. The authors also found that organic matter is responsible for tight binding of copper as determined by an extraction method for inorganically and organically bound copper. In comparison with other metals, the adsorption potential for copper is superseded only by iron; it is greater than that found for Cr, Zn, Pb, Cd, Hg and Ni (Patterson, 1978).

Sludge Disposal: Sludge that is disposed of on land may go to a sanitary landfill, or be spread for the purpose of amending the soil. The form of copper in sludge is not exactly known. Sommers et al. (1976) detected no copper sulfides, phosphates, or hydroxides in sludges containing relatively high concentrations of copper. They did find a copper-hydroxy-carbonate complex, and suggested that the chemistry of copper in sludge is relatively complicated. The same study found that the movement of copper in sludge-amended soils was unaffected by the soil type, pH or clay content. Minimal movement of heavy metals was observed in the top 7.5 cm of soil, and no translocation was detected between 7.5 cm and 15 cm. The authors concluded that the application of sludge to soils does not enhance the solubility or movement of copper.

The concentration of copper found in leachate from cropland amended with sewage sludge was found to be a function of the magnitude of the initial copper loading (CAST, 1976). For instance, leachate from a sludge loading of 11.3 kg Cu/ha at a 15-cm and 120-cm soil depth contained higher concentraions of Cu than the control at a depth of 15 cm. Even so, the amount of copper moving past the 120-cm depth is not expected to exceed 0.3% and 0.5% of the initial copper loading for the high and low treatments, respectively; the concentration of dissolved copper in the leachate was in all cases less than 12 μg/L.

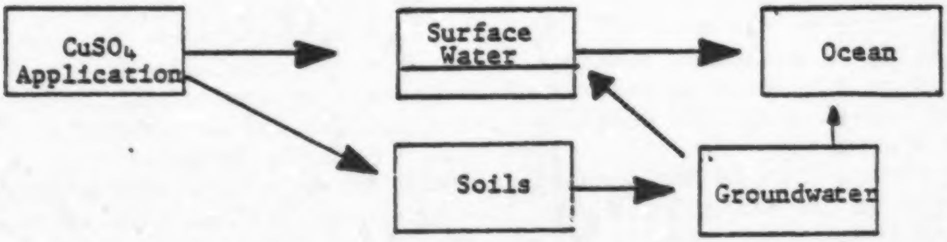
The copper in sewage sludges and other wastes disposed of in sanitary landfills may be more mobile than the case described above for soil application. Data on the mobility and concentrations of copper in leachate from landfills accepting sewage sludges were not available for this study. The studies discussed in Pathway #2 indicate a typical copper concentration of 0.04-0.4 mg/L in leachate from municipal refuse landfills. Under proper operating conditions, copper will quickly be attenuated by the soil. Sludge that is incinerated will contribute to the concentrations of copper in the atmosphere. The fate processes will be similar to the chain of events described in Pathway #1.

Surface Water Discharge: A survey of 192 POTW's showed effluent copper concentrations ranging from 0.003 mg/L to 1.8 mg/L, with a mean of 0.126 mg/L and associated standard deviation of 0.242 mg/L (U.S. EPA, 1979a). The behavior of copper discharged with POTW effluents into local surface waters will be similar to that already described for aqueous pathways (Pathway #3); concentrations will be rapidly reduced through adsorption and dilution. The fate of copper discharged by the Joint Water Pollution Control Project (JWPCP) of the Los Angeles County Sanitation District has been studied in some detail (Morel et al., 1975), and may be generally representative of POTW discharges to the ocean.* While copper was found in the fairly insoluble sulfide form in the effluent (~370 million gallons per day effluent, discharged through submarine outfalls at a depth of 60 m), the studies indicated that the combined processes of dilution and oxidation resulted in substantial solubilization of copper (as well as other metals); this increases the residence time of metals in the water and allows them to be transported greater distances where the effects on background copper concentrations would be negligible. It was estimated that only about 1% of the metals were deposited in the general area of the outfall. The sediments that do settle near the outfall are likely to be anoxic (Bertine and Goldberg, 1977) and copper would thus be in the sulfide form. The point source discharges of wastewater were initially diluted by a factor of 100, followed by a five-fold dilution in one tidal cycle. Similarly, outfall was at or below the concentrations found in the open ocean (Schell and Nevissi, 1977).

Summary: The concentration of copper in POTW effluent, and the effectiveness of its removal is dependent upon the initial influent concentration and type of treatment inacted. There is evidence that industrial waste pretreatment reduces the concentration of copper in POTW effluents (both wastewaters and sludges). Most of the copper is partitioned into the sludge portion of sewage during treatment. Sludge spread for the purposes of soil amendment does not enhance the solubility or mobility of copper. Copper is expected to be attenuated quickly in the soil. Copper in aqueous effluents will be adsorbed to sediment and particulate, and be diluted. Discharge to marine system causes solubilization of copper, prohibiting localized "hot-spots" in the sediments.

f. Copper Sulfate Use

Pathway #5



---

*The wastes, containing both domestic and industrial wastes, contain high levels of copper (560 mg/L) after primary treatment.

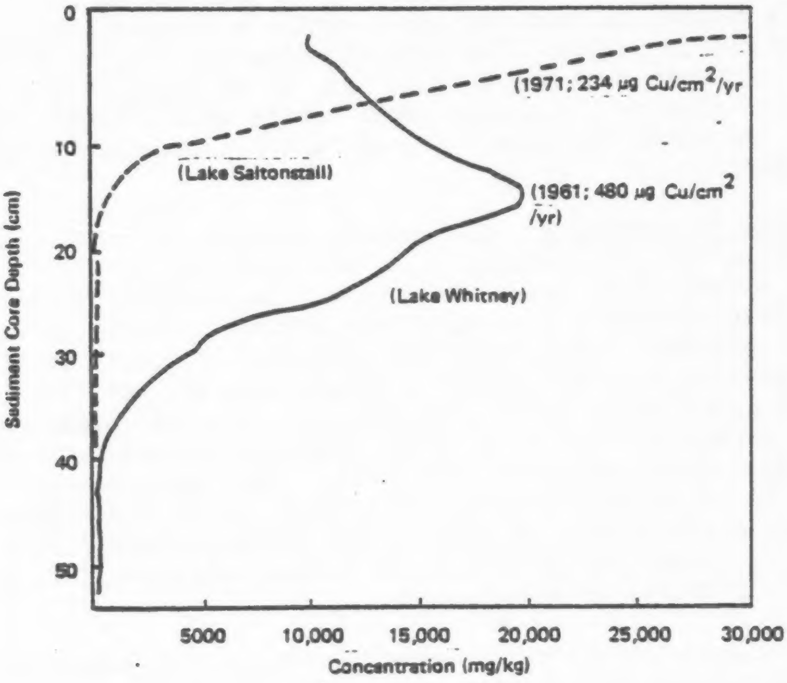
Copper sulfate is used for agricultural purposes as a fungicide, feed, and fertilizer for citrus fruits, deciduous fruits, and vegetables. In water bodies, it is used as an algicide.

Fate of Dissolved Copper: Copper dispersal in a water body has been studied with regard to its use as an algicide (Button et al., 1977). The experiment consisted of putting 0.2g $Cu^{2+}/m^2$and 0.4gCu^{2+}/m^2 into a reservoir with a pH of 7.3-7.8 and fairly hard water. All but 5% of the $CuSO_4$ was dissolved within the top 1.75 m of water Within 2.5 hrs the concentration of soluble copper returned to baseline values; for 0.4g Cu^{2+}/m^2, baseline levels were evident after 24 hrs. The decrease in soluble copper was accompanied by an increase in particulate copper. This is caused, in part, by the sorption of copper to plankton, which settled to the bottom. The effectiveness of $CuSO_4$ as an algicide was demonstrated by applying 0.4g Cu^{2+}/m^2 to an algal bloom consisting mostly of diatoms. Although toxic levels were present for only a few hours, the bloom was controlled and did not reappear over the course of the summer.

Fate in Sediments: The binding capacity of the sediments for copper was studied in Lake Monona, which had received 1.5 x 10^6 lb. of $CuSO_4$ within a span of 50 years (Sanchez and Lee, 1973). These authors found that carbonate alkalinity was proportional to the binding capacity of the sediments. The authors suggested that copper replaced calcium and magnesium ions within the carbonate crystal lattice. The authors did not investigate binding to organics, iron and manganese oxides or clays. Other studies cited found that copper could not be leached from Lake Monona sediments with 0.1 N HCl. This implies that copper is not easily desorbed from whatever it is bound to in the sediments. Two successive extractions with 1.0 N HCl released only 71% of the added copper; at least 29% of the copper is not, therefore, in a form accessible for biotic uptake or dissolution.

Another study of two reservoirs outside New Haven, Connecticut, found that the pattern of concentration of copper in the sediments closely parallels that of $CuSO_4$ use (Bertine and Mendeck, 1978). The range of copper sulfate additions to the reservoirs since 1935 spans 1000 kg to 10,000 kg per year. For both lakes, the sediment depth of the highest copper concentration corresponds to the year of greatest use; for Lake Whitney, the year was 1961, corresponding to a 15-cm depth, for Lake Saltonstall, the year was 1971, near the top 5 cm. Figure 17 illustrates the copper concentration in the sediments vs. depth.

Summary: Copper sulfate appears to be an effective algicidal agent within a very short time frame. The concentrations of copper ion in the water column are returned to background levels within a day of application. The copper sorbs to particulates (in this case, algae) and sediments. Concentrations in core samples of sediment reflect the use of $CuSO_4$ over the years.



Reference: Bertine and Mendeck (1978)

FIGURE 17. COPPER CONCENTRATION IN RESERVOIR SEDIMENT VS. SEDIMENT DEPTH

3. Biological Pathways

This section considers the fate of copper in biological systems. Uptake and bioaccumulation have been considered.

Copper is accumulated in the tissues of fresh and salt water fish and invertebrate species to concentrations greater than those measured in the surrounding water. Tables 13 and 14 present reported copper bioconcentration ratios (concentration of Cu in the organism divided by concentration of Cu in water) in various aquatic species and, when available, Cu concentrations in the surrounding water. The levels accumulated are dependent primarily upon those environmental factors affecting the availability of the cupric ion. Particularly important are pH (which affects the degree of complexing by organic and inorganic ligands) and water hardness. It has been hypothesized that there is less uptake at low pH because of reduction in electrostatic forces of negatively charged groups in cell membranes (Wright and Diamond, 1968; Mierle and Stokes, 1976), and because less ionic copper is available for uptake. Water hardness affects uptake by reducing adsorption at relatively high concentrations of Ca^{++} (Mierle and Stokes, 1976).

In two algal species, *Scendesmus acuminatus* and *Scendesmus acutiformis*, copper uptake occurs through (1) adsorption to the cell wall and (2) transport via diffusion across the cell wall, followed by binding, probably to sulfhydryl ligands (Mierle and Stokes, 1976). Different species appear to have different propensities for uptake. Bioconcentration ratios can range from 12 to 3040 for various algal species (Table 13).

Aquatic invertebrate species, both fresh and salt water, accumulate copper in their body tissues and shells. Copper is an important trace element in the heme pigment of molluscs (Greig, 1979). Accumulation occurs through uptake of copper adsorbed to particulates or sediment containing copper residues, as well as directly from soluble forms in the water column (Greig and Wenzloff, 1978). The Atlantic Oyster has accumulated copper levels one order of magnitude higher than concentrations dissolved in water (Shuster and Pringle, 1969 as cited in Phillips and Russo, 1979). Uptake in this species continued until a plateau concentration of 200 mg/kg was reached after approximately 30 weeks. Copper is concentrated by the mucous sheets of the oyster, leading one author to suggest that intake of particulates may be the primary mode of uptake (Pringle, *et al.*, 1968 as cited in Grieg, 1979). In the mussel, *Mytilus edulus*, tissue concentrations of copper decreased with increased mucous excretion (Scott and Major, 1972, as cited in Phillips and Russo, 1978). The excreted copper was unavailable for reaccumulation under the static conditions in which the experiment was conducted; however, in an experiment providing a continual inflow of copper, the lost metal may be replaced through further uptake. In fresh water clams, copper concentrations reached levels several orders of magnitude higher than copper concentrations in water, but slightly lower than those measured in sediments (Anderson, 1973; Mathis and Cummings, 1973). Levels were highest in gill

TABLE 13. BIOCONCENTRATION FACTORS FOR ALGAE AND AQUATIC INVERTEBRATES

	F or L^1	Bioconcentration Factor/Ratio	Aqueous Conc. (mg/L)	Duration	Reference
Algae					
Scenedesmus sp.	-	2,400	-	-	Stokes et al. (1973)^2
Scenedesmus sp.	L	<1,000-2,000 (day)	-	1-60 min	Mierle and Stokes (1976)
Scenedesmus guadricavda	-	12	-	-	Khobotév et al. (1976)^2
Anabaena variabilis	-	300	-	-	Khobotév et al. (1976)^2
Chorella sp.	-	2,400	-	-	Stokes et al. (1973)^2
Plants, marine and fresh	-	1,000	-	-	EPA (1977a)^2
Invertebrates					
Tubificids	F	8,077	0.0052	-	Mathis and Cummings (1973)
Chironomid larvae	F	546	1.91	-	Namminga and Wilhm (1977)
Polychaete (Nereis sp.)	F	32.27	1.31	-	Guthrie et al. (1979)
Barnacle (Balanus aburneus)	F	11.66	1.31	-	Guthrie et al. (1979)
Crab (Callinectes sapidus)	F	2.28	1.31	-	Guthrie et al. (1979)
Oyster (Crassostrea virginica)	F	31.04	1.31	-	Guthrie et al. (1979)
Oyster (Crassostrea virginica)	L	28,000	0.025	20 wks	Shuster and Pringle (1969)
Clam (Rangea cuneata)	F	17.37	1.31	-	Guthrie et al. (1979)
Hardshell clam (Mercenaria mercenaria)	-	30,000	-	-	Raymont (1972)^2
Clams (3 species)	F	692	0.0052	-	Mathis and Cummings (1973)

Reproduced from best available copy.

Reproduced from best available copy.

TABLE 13 (CONTINUED)

	F or L[1]	Bioconcentration Factor/Ratio	Aqueous Conc. (mg/L)	Duration	Reference
Mussel (*Mytilus galloprovincialis*)	-	184	-	-	Majori and Petronio (1974)
Freshwater invertebrates	-	1,000	-	-	U.S. EPA (1977a); Ross (1977)[2]
Squid (3 species)	F	21×10^6	0.007	-	Martin and Flegal (1975) as cited in Phillips and Russo (1978)
Marine invertebrates	-	1,670	-	-	U.S. EPA (1977a); Ross (1977)[2]
viscera	-	5,000	-	-	U.S. EPA (1977a)[2]

---

[1] F = Field study; L = Laboratory study

[2] As cited in Versar (1979b)

TABLE 14. BIOCENCENTRATION IN FISH

Species	F or L[1]	Bioconcentration Factor/Ratio	Aqueous Conc. (mg/L)	Duration	Reference
Brown bullhead (Ictalurus nebulosus)	L	~500-3,000	0.027	30 days	Brungs et al. (1973)
Brook trout (Salvelinus fontinalis)	L	~1	0.0094	-	McKim and Benoit (1974) as cited in Phillips and Russo (1978)
Rainbow trout (Salmo gairdneri)	-	signif. accum.	0.003	107 wks	Goettl, et al. (1974) as cited in Phillips and Russo (1978)
Fish					
Marine	-	667	-	-	U.S. EPA (1977a); Ross (1977a)[2]
Fresh	-	50-200; 200	-	-	U.S. EPA (1977a); Ross (1977a)[2]
Fish (10 species)	F	~78.8 (ave.)	0.0052	-	Mathis and Cummings (1973)

---

[1] F = Field Study; L - Lab Study

[2] As cited in Versar (1979b)

Reproduced from best available copy.

tissue, followed by the viscera (implicating uptake through ingestion) and the muscle, with the lowest concentration measured in the shell (Anderson, 1973). In a microcosm study, copper concentrations were approximately one order of magnitude greater in five estuarine invertebrate species [oyster (Crassostrea virginica), barnacle (Balanus aburneus), clam (Rangia cuneata), blue crab (Callinectes sapidus), and polychaete (Nereis sp.)] than concentrations in water (Greig, 1979). Concentrations in the sediment, however, were higher than concentrations measured in the organisms by one order of magnitude. Three species of squid (Loligo opalescens, Ommastrephes bartrami, and Symplectoteuthis oualaniensis) were found to concentrate copper in their livers up to six orders of magnitude over concentrations in water (Martin and Flegal, 1975, as cited in Phillips and Russo, 1978). The authors suggested that the high levels were due to copper requirements for metabolic processes in squid.

Lower invertebrates, chironomids and tubificids also showed tissue copper concentrations higher than water concentrations (by two to four orders of magnitude) but equal to or lower than sediment concentrations in field studies (Namminga and Wilhm, 1977; Mathis and Cummings, 1973).

Fish species have been shown to accumulate copper in their tissues (Table 14); however, bioaccumulation may depend on the concentration to which they are exposed. For example, McKim and Benoit (1974) found no copper uptake by brook trout at a concentration of 9.4 μg/L in water. On the other hand, Goettel et al. (1974, as cited in Phillips and Russo, 1978) reported that rainbow trout accumulate copper in the liver when exposed to concentrations in water of 3 μg/L. Other species reported to accumulate copper in various tissues are bluegill (Benoit, 1975), brown bullhead (Brungs et al., 1973), stone loach (Solbé and Cooper, 1976), and mummichog (Eisler and Gardner, 1973 as cited in Phillips and Russo, 1978). The liver apparently is a common site for copper concentration in fish, often containing the highest copper levels of all tissues in the body, and is more apt to retain copper when the organism is removed from contaminated water and placed in clean water (Solbé and Cooper, 1976). In a field study, ten species of fish were found to accumulate copper at a concentration one to two orders of magnitude greater than the water concentrations, but one to two orders lower than sediment concentrations (Mathis and Cummings, 1973).

Plants in general require some copper for metabolic processes. The amount required varies among species. Concentrations of copper in plant tissue at less than 5 μg/g (dry weight) probably indicate a deficiency (NRC, 1977). Copper is one of the least available of the essential nutrients (NRC, 1977), and deficiency problems are common in some parts of the U.S. Background concentrations of copper in crops grown in mineral soil (presumably where copper is abundant) range from 1 mg/kg to over 50 mg/kg (dry weight). Beeson (1941) and NRC (1977) provide a more detailed discussion of background levels in crops.

The amount available for uptake by plants often differs considerably from the total copper content in soil. Factors that influence availability include pH, clay content, microbial activity, moisture, and organic content, and the concentrations of phosphate, manganese, and zinc, which apparently compete with copper for transport sites on plant roots (NRC, 1977). As a result, concentrations of copper in plants are considered by some to be independent of copper concentrations in soil (Timperley et al., 1977, as cited in EPA, 1979b). Various crops growing in sewage-sludge treated fields with soil copper concentrations of up to 280 mg/kg, had copper concentrations (in the utilizable part of the plant) similar to concentrations in plants grown in non-treated soil (Dietz and Rosopulo, 1976, as cited in EPA, 1979b). Leaves and stalks, however, had concentrations approaching toxic levels for livestock. An application to soil of 164 kg of copper per hectare in domestic waste water sludge had different effects on different crop species (CAST, 1976). Tissue concentrations increased from 7.7 mg/kg to 14.4 mg/kg in cucumbers and from 7.5 mg/kg to 12.2 mg/kg in broccoli. On the other hand, concentrations in potatoes did not change. There was no consistent trend in the location of copper.

Some typical copper residues measured in plants, both crop and wild species, growing in the vicinity of anthropogenic sources of copper were presented previously in Section IV-A.

In conclusion, copper is accumulated by biota to various degrees. Where unusually high concentrations of copper are available in soil or water, tissue concentrations of Cu may increase over background levels, depending on the species exposed. Bioconcentration factors in aquatic organisms range from less than one to six orders of magnitude higher than water concentrations. High bioaccumulation potential may be due to greater metabolic requirements for copper. The limited information on bioconcentration factors in plants indicatesranges of from one to three orders of magnitude over water levels for algae and for terrestrial plants ranges of from one to three orders of magnitude higher than soil concentrations. Little information was available on the contribution of background levels of copper to these bioconcentration factors. Limited information available suggests that copper is not biomagnified in food chains.

C. SUMMARY

1. Distribution

Ambient copper levels in seawater generally range between 1 μg/L and 5 μg/L. STORET data for U.S. major river basins indicate that most observations of total copper were between 1 μg/L and 100 μg/L. The major basins with the highest percentage of samples with concentrations exceeding 100 μg/L are the New England, Western Gulf and Lower Colorado regions.

STORET data on sediment concentrations in the major river basins are in the range of 1 mg/kg to 1,000 mg/kg which are two to four orders of magnitude greater than concentrations found in river water. The highest mean copper levels in sediments are found in Hawaii, the Lower Colorado River, the Upper Mississippi Valley and the Great Lakes.

STORET also provided the most comprehensive compilation of copper residues in freshwater fish tissues. The majority of the samples had concentrations between 1 mg/kg and 10 mg/kg. Hawaii, Puerto Rico and the Colorado River Basin had the highest mean residues among the STORET regions. Marine species had residues similar to those of freshwater species, except for oysters, which sometimes had copper levels exceeding 1,000 mg/kg.

Copper is an essential micronutrient for plants, and appears in concentrations of 4-15 mg/kg in edible species. Copper occurs naturally at concentrations of 50 mg/kg in the earth's crust, although parent materials such as biotite and pyroxene basalts average 140 mg/kg copper. Airborne concentrations of copper in rural and urban areas normally range from 0.01 $\mu g/m^3$ to 0.3 $\mu g/m^3$. Levels as high as 2 $\mu g/m^3$ have been measured near a copper smelter.

2. General Fate

The speciation and concentration of copper in the water column is a function of numerous parameters. Generally, however, an aerated water system will contain the aqueous carbonate and hydroxide species above pH 7, and the divalent ion below this pH. Copper exhibits a great tendency toward adsorption to the extent that it exceeds other divalent metal ions in this capacity. Therefore, one finds it sorbed to sub-micron particulate matter in the sediments, and suspended solids of aqueous systems, as well as to the particulate matter in air and soils. Hydrous iron and manganese oxides, clays and organic matter serve as sorption sites.

In soils, sorption of copper occurs above pH 5. Below this level, translocation of copper as the divalent ion becomes possible.

3. Specific Pathways

a. Air

Point source combustion sources are the primary contributors of copper to the atmosphere. Copper is emitted as a vapor, oxide and sorbed to sub-micron particulates No clear evidence exists for the role air-pollution control devices play in the regulation of copper emissions to the atmosphere. Wet and dry fallout results in localized increases to the copper concentrations found in nearby soils, surface waters and urban pavement. The concentration of copper in urban runoff has been noted to contribute significantly to ultimate discharge into surface waters.

b. Solid Waste

The land receives the bulk of copper resulting from anthropogenic sources. Hazardous and municipal waste sites that receive copper-containing sludges have been found to average about 0.04-0.4 mg/L of copper in the leachate. Acid mine drainage from abandoned mines causes initial spikes in the surface water copper concentrations. The stream's recovery is a function of distance downstream.

c. Industrial Wastewater

Pretreatment of industrial wastewaters of the metal finishing industry resulted in lower concentrations discharged to surface waters and concentrated copper-containing sludges destined for landfill disposal. Surface water sediments are the best indicators of industrial discharge; remaining copper in the water column is ultimately destined for lake or ocean sediments.

d. POTW's

Copper removal from POTW influents is affected by the treatment scheme, and incoming copper concentration. Industrial wastewater pretreatment was necessary to ensure effective removal of copper during treatment at the POTW in several cases. The copper partitions into the sludge portions of the waste during treatment. Land disposal (agricultural or municipal landfill) does not appear to render copper mobile from the sludge. Incineration of the sludge contributes to the concentrations of copper in the air.

e. Copper Sulfate Use

Use of copper sulfate as an algicide in reservoirs and other surface waters increases the concentration of copper in sediments. The concentration of the divalent ion resumes background levels with 1 day of application.

4. Biological Pathways

Copper is accumulated by biota to various degrees, depending on the concentration in the medium and environmental conditions. For aquatic organisms, high hardness and pH tend to promote accumulation. Bioconcentration factors can be up to six orders of magnitude greater than water concentrations. Plants may also take up copper to levels up to three orders of magnitude over soil concentrations.

REFERENCES

Allaway, W.H. 1974. Agronomic controls over the environmental cycling of trace elements. Adv. Agronomy 20:235-275.

Anderson, R.V. 1973. Concentration of cadmium, copper, lead and zinc in six species of freshwater clams. Bull. of Env. Contam. Toxicol. 18(4): 492-496.

Anon. 1977. U.S. Environmental Protection Agency. Copper-computer printout. Office of Oil and Hazardous Materials - Technical Assistance Data System, Washington, D.C. 3p.

Beeson, K.C. 1941. The mineral composition of crops with particular reference to the soils in which they were grown. A review and compilation. U.S. Department of Agriculture Miscellaneous Publication 369. U.S. Government Printing Office, Washington, D.C.

Benoit, D.A. 1975. Chronic effects of copper on survival, growth, and reproduction of the Bluegill (*Lepomis macrochirus*). Trans. of the Amer. Fish. Soc. 104(2):353-358.

Berger, K.C. 1976. Sun, Soil and Survival. University of Oklahoma Press.

Bertine, K.K. and E.D. Goldberg. 1977. History of heavy metal pollution - Southern California coastal zone - reprise. Environ. Sci. Technol. 11(3): 297-299.

Bertine, K.K. and M.F. Mendeck. 1978. Industrialization of New Haven, Conn., as recorded in reservoir sediments. Environ. Sci. Technol. 12(2):201-207.

Biener, J.A. and W.H. Bourma. 1978. Case history of city of Grand Rapids, Michigan program of industrial waste control. Pretreatment of industrial wastes - Joint Municipal and Industrial Seminar, A.S. Vernick, H.D. Feiler, P.D. Lanik, (Eds.) EPA Seminar Handout.

Bruland, K.W., K. Bertine, M. Koide, and E.D. Goldberg. 1974. History of metal pollution - Southern California coastal zone. Environ. Sci. Technol. 8(5):425-432.

Brungs, W.A., E.N. Leonard, and J.M. McKim. 1973. Acute and long-term accumulation of copper by the brown bullhead, *Ictalurus nebulosus*. Journ. Fish. Res. Bd. Can. 30:583-586.

Button, K.S., H.P. Hostetter and D.M. Mair. 1977. Copper dispersal in a water-supply reservoir. Water Research. 11(7):539-544.

Cataldo, D.A. and R.E. Wilding. 1978. Soil and plant factors influencing the accumulation of heavy metals by plants. Environ. Health Perspectives 27:149-159.

Chian, E.S.K. and F.B. DeWalle. 1977. Evaluation of leachate treatment. Vol. 1, Characterization of leachate. U.S. EPA, Office of Research and Development. EPA-6001/2-77-186a.

Chu, T-Y., G.R. Steiner, C.C. McEntyre. 1978. Removal of complex copper-ammonia ions from aqueous wastes with fly ash. J. Water Poll. Control Fed. 50(9):2157-2174.

Coles, D.G., R.C. Ragaini, J.H. Ondor, G.L. Fisher, D. Silberman, and B.A. Prentice. 1979. Chemical studies of fly ash from a coal-fired power plant. Environ. Sci. Techn. 13(4):455-459.

Council for Agricultural Science and Technology (CAST). 1976. Application of sewage sludge to cropland: Appraisal of potential hazards of the heavy metals to plants and animals. Prepared for U.S. EPA, Office of Water Program Operations EPA-430/9-76-013.

Davis, J. and J. Jacknow. 1975. Heavy metals in wastewater in three urban areas. J. Water Pollut. Control Fed. 47(9):2292-2297.

Davis, J.A. and J.O. Leckie. 1978. Effects of absorbed complexing ligands on trace metal uptake by hydrous oxides. Environ. Sci. Technol. 12(12): 1309-1315.

Delfino, J.S. 1977. Effects of river discharge and suspended sediment on water quality in the Mississippi River. J. Environ. Sci. Health. A12(3): 79-94.

Dietz, V.T. and A. Rosopulo. 1976. Schwermetallgehalte in Boden und Pflanzen nach extrem hohen Klairschlammgabe. Landwirtsch. Forsch. 33:236-248 (In German with English summary), as cited in Versar (1979).

Duce, R.A., J.G. Quinn, C.E. Olney and S.R. Piotrowicz. 1972, Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island. Science. 176(14):161-163.

Eaton, A. 1979. Observations of the geochemistry of soluble copper, iron, nickel and zinc in the San Francisco Bay estuary. Environ. Sci. Technol. 13(4):425-432.

Elzerman, A.W., D.E. Armstrong and A.W. Andren. 1979. Particulate zinc, cadmium, lead, and copper in the surface microlayer of Southern Lake Michigan. Environ. Sci. Technol. 13(6):720-725.

Fink, Jr., L.K., D.M. Pope, A.B. Harris, and L.L. Schick. 1976. Land and Water Resources Institute. University of Maine at Orono. (PB-263 497)

Cataldo, D.A. and R.E. Wilding. 1978. Soil and plant factors influencing the accumulation of heavy metals by plants. Environ. Health Perspectives 27:149-159.

Chian, E.S.K. and F.B. DeWalle. 1977. Evaluation of leachate treatment. Vol. 1, Characterization of leachate. U.S. EPA, Office of Research and Development. EPA-6001/2-77-186a.

Chu, T-Y., G.R. Steiner, C.C. McEntyre. 1978. Removal of complex copper-ammonia ions from aqueous wastes with fly ash. J. Water Poll. Control Fed. 50(9):2157-2174.

Coles, D.G., R.C. Ragaini, J.H. Ondor, G.L. Fisher, D. Silberman, and B.A. Prentice. 1979. Chemical studies of fly ash from a coal-fired power plant. Environ. Sci. Techn. 13(4):455-459.

Council for Agricultural Science and Technology (CAST). 1976. Application of sewage sludge to cropland: Appraisal of potential hazards of the heavy metals to plants and animals. Prepared for U.S. EPA, Office of Water Program Operations EPA-430/9-76-013.

Davis, J. and J. Jacknow. 1975. Heavy metals in wastewater in three urban areas. J. Water Pollut. Control Fed. 47(9):2292-2297.

Davis, J.A. and J.O. Leckie. 1978. Effects of absorbed complexing ligands on trace metal uptake by hydrous oxides. Environ. Sci. Technol. 12(12): 1309-1315.

Delfino, J.S. 1977. Effects of river discharge and suspended sediment on water quality in the Mississippi River. J. Environ. Sci. Health. A12(3): 79-94.

Dietz, V.T. and A. Rosopulo. 1976. Schwermetallgehalte in Boden und Pflanzen nach extrem hohen Klairschlammgabe. Landwirtsch. Forsch. 33:236-248 (In German with English summary), as cited in Versar (1979).

Duce, R.A., J.G. Quinn, C.E. Olney and S.R. Piotrowicz. 1972, Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island. Science. 176(14):161-163.

Eaton, A. 1979. Observations of the geochemistry of soluble copper, iron, nickel and zinc in the San Francisco Bay estuary. Environ. Sci. Technol. 13(4):425-432.

Elzerman, A.W., D.E. Armstrong and A.W. Andren. 1979. Particulate zinc, cadmium, lead, and copper in the surface microlayer of Southern Lake Michigan. Environ. Sci. Technol. 13(6):720-725.

Fink, Jr., L.K., D.M. Pope, A.B. Harris, and L.L. Schick. 1976. Land and Water Resources Institute. University of Maine at Orono. (PB-263 497)

Friberg, L., *et al*. 1977. *Toxicology of Metals - Volume II*, EPA-600/1-77-022.

Greig, R.A. and D.R. Wenzloff. 1978. Metal accumulation and depuration by the American Oyster, *Crassostrea virginica*. Bull. Environ. Contam. Toxicol. 20:499-504.

Greig, R.A. 1979. Trace metal uptake by three species of mollusks. Bull. Environ. Contam. Toxicol. 22:643-647.

Grimwood, C. and T.J. McGhee. 1979. Prediction of pollutant release resulting from dredging. J. Water Pollution Control. Fed. 51(7):1811-1815.

Guthrie, R.E., E.M. Davis, D.S. Cherry, and H.E. Murray. 1979. Biomagnification of heavy metals by organisms in a marine microcosm. Bull. Environ. Contam. Toxicol. 21:53-61.

Holcombe, L.A. 1977. Adsorption and desorption in mine drainages. NTIS PB-290 614/7WP.

Huang, C.P., H.A. Elliott, and R.M. Ashead. 1977. Interfacial reactions and the fate of heavy metals in soil-water systems. J. Water Poll. Control Fed. 49(5):745-756.

Jacko, R.B. and D.W. Neuendorf. 1977. Trace metal particulate emission test results from a number of industrial and municipal plant sources. J. Air Pollution Assoc. 27(10):989-994.

Jacko, R.B., D.W. Neuendorf, and F. Faure. 1976. Fractional collection efficiency of electrostatic precipitator for open hearth furnace trace metal emissions. Environ. Sci. Technol. 10(10):1002-1005.

Jacko, R.B., D.W. Neuendorf., and K.J. Yost. 1975. Trace metal emissions from a scrubber controlled municipal incinerator. ASME Paper #N75-WA/APC-2.

Khobot´ev, V.G., V.I. Kapkov, E.G. Rukhodze, N.V. Turunina, and N.A. Shidlovskaya. 1976. Copper uptake by algae from copper-containing compounds and the effect of this process on their salt metabolism. Gidrobiol. Zh. 12(1):40-46 (Russian).

Kleinman, M.T., T.J. Knelp, D.M. Bernstein, and M. Eisenbud. 1977. Fallout of toxic metals in New York City. *Biological Implications of Metals in the Environment*. H. Drucker and R.E. Wildung (Eds.). Technical Information Center, Energy Research and Development Administration.

Kubota, J., E.L. Mills, and R.T. Oglesby. 1974. Lead, cadmium, zinc, copper and cobalt in streams and lake waters of Cayuga Lake Basin, New York. Environ. Sci. Technol. 8(3):243-248.

Majori, L. and F. Petronio. 1973. Accumulation phenomenon which takes place in a mussel (Mytilus galloprovincialis LMK) grown in an artificially polluted environment. II. Pollution from copper. Ig. Mod. 66(1):64-78 (Italian)

Martin, H.W. and W.R. Mills, Jr. 1976. Water pollution caused by inactive ore and mineral mines - a national assessment. NTIS #PB-264 956. Prepared for the Office of Research & Development, U.S. EPA, Cincinnati, OH

Mathis, B.J. and T.F. Cummings. 1973. Selected metals in sediments, water, and biota in the Illinois River. Water Pollution Control Fed. 45(7):1573-1583.

McKim, J.M. and D.A. Benoit. 1974. Duration of toxicity tests for establishing "No Effect" concentrations for copper with brook trout (Salvelinus fontinalis). Fish. Res. Bd. Can. 31(4):449-451.

Mezey, E.J., S. Singh, and D.W. Hissong. 1976. Fuel Contaminants: Vol. 1 Chemistry. Report by Battelle-Columbus Laboratories to the EPA, Office of Research & Development (EPA-600/2-76-177a; PB-256 020)

Mierle, G. and P.M. Stokes. 1976. Heavy metal tolerance and metal accumulation by planktonic algae. Trace Substances in Environmental Health. D.D. Hemphill (Ed.), Proc. Symp., Columbia, Mo; Univ. of Mo.

Milanovich, F.P., R. Spies, M.S. Guram, and E.E. Sykes. 1976. Uptake of copper by the polychaete Cirriformia spirabrancha in the presence of dissolved yellow organic matter of natural origin. Est. Coast. Mar. Sci. 4(5):585-588.

Morel, F., R.E. McDuff, and J.J. Morgan. 1973. Interactions and Chemostasis in aquatic chemical systems: Role of pH, pE, Solubility and complexation. Trace Metals and Metal Organic Interaction in Natural Waters. Phillip C. Singer (Ed.), Ann Arbor Science, Ann Arbor, MI

Morel, F.M.M., J.C. Westall, C.R. O'Melia, and J.J. Morgan. 1975. Fate of trace metals in Los Angeles County wastewater discharge. Environ. Sci. Technol. 9(8):756-761

Mytelka, A.I., J.S. Czachov, W.B. Guggino, and H. Golub. 1973. Heavy metals in wastewater and treatment plant effluent. J. Water Pollution Control Fed. 45(9):1859-1864.

Namminga, H. and J. Wilhm. 1977. Heavy metals in water, sediments and chironomids. J. Water Pollution Control Fed. 49(7)1725-1731.

National Academy of Sciences. 1977. Copper, subcommittee on copper committee on medical and biologic effects of environmental pollutants." national research council, EPA-600/1-77-003, Washington, D.C.

National Research Council (NRC). 1977. Copper. (PB-262 425)

Patterson, J.W. 1978. Heavy metals removal in combined wastewater treatment. Presented at International Environment Colloquium, University of Liege, Belgium, May 16-19

Perhac, R.M.. 1974. Water transport of heavy metals in solution and by different sizes of particulate solids. (NTIS #PB-232 427)

Peyton, T. and A. McIntosh. 1974. A field study on the distribution of aerially deposited trace elements in an aquatic ecosystem I Sediment component. Trace Subst. Environ. Health. 8:193-201

Phillips, G.R. and R.C. Russo. 1978. Metal bioaccumulation in fishes and aquatic invertebrates: A literature review. US EPA-600/3-78-103

Pringle, B.H., D.E. Hissong, E.L. Katz, and S.T. Mulawka. 1968. A.S.C.E. Proc. J. Sanit. Engineer. Div. 94 (Sa3) pp. 455

Ragaini, R.C., H.R. Ralston, and N. Roberts. 1977. Environmental trace metal contamination in Kellogg, Idaho near a lead smelting complex. Environ. Sci. Technol. 11(8):773-784

Raymont, J.E.G. 1972. Pollution in Southhampton water. Proc. Roy. Soc. Ser. B. 180(1061):451-468

Ross, R.H. 1977. Environmental interactions. *Environmental, health, and control aspects of coal conversion: An information overview*. pp. 6-98. Braunstein, H.M., E.D. Copenhaver, and H.A. Pfuderer (Eds.). Oak Ridge National Lab, Oak Ridge, TN.

Roulier, M.H. 1975. Research on contaminant movement in soils. Paper presented at NATO/CCMS meeting on landfill research, London, England, Oct. 20-22.

Sagik, B.P. and C.A. Sorber. 1977. *Risk Assessment and Health Effects of Land Application of Municipal Wastewater and Sludges*. Proceedings of Conference, Dec. 12-14, 1977, Center for Applied Research Technology, University of Texas, San Antonio.

Sanchez, I., and G.F. Lee. 1973. Sorption of copper on Lake Monona sediments - effect of NTA on copper release from sediments. Water Research. 75:87-593.

Schell, W.R. and A. Nevissi. 1977. Heavy metals from waste disposal in central Puget Sound. Envir. Sci. Tech. 11(9):887-893.

Serne, R.J. 1977. Geochemical distribution of selected trace metals in San Francisco Bay sediments. In: Biological Implications of Metals in the Environment. H. Drucker and R.E. Wildung (Eds.). Technical Information Center, Energy Research and Development Administration.

Solbé, J.F. de L.G. and V.A. Cooper. 1976. Studies on the toxicity of copper sulphate to stone loach Noemacheilus barbatulus (L.). Water Res. 10:523-527.

Sommers, L.E., D.W. Nelson, R.E. Terry, and D. J. Silviera. 1976. Nitrogen and metal contamination of natural waters from sewage sludge disposal on land. Purdue University Water Resources Research Center, #89.

Stiff, M.J. 1971. The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. Water Res. 5:585-599.

Stoffers, P., C. Summerhayes, V. Forstner, and S.R. Patchineelam. 1977. Copper and other heavy metal contamination in sediments from New Bedford Harbor, Massachusetts: A preliminary note. Environ. Sci. Technol. 11(8):819-821.

Stokes, P.M., T.C. Hutchinson, and K. Krauter. 1973. Heavy metal tolerance in algae isolated from polluted lakes near the Sudbury, Ontario smelters. Water Poll. Res. Can. 8:178-201.

Stumm, W. and J. J. Morgan. 1970. Aquatic chemistry. Wiley-Interscience, New York.

Sverdrup & Parcel and Associates, Inc. 1977. Study of selected pollutant parameters in publicly owned treatment works (Draft) - Task Order No. 7 under EPA Contract 68-01-3289.

Theis, T.L. and R.O. Richter. 1979. Chemical speciations of heavy metals in power plants ash pond leachate. Environ. Sci. Technol. 12:1302-1308.

Timperley, M.H., R.R. Brooks, and P.J. Peterson. 1977. The significance of essential and non-essential trace elements in plants in relation to biogeochemical prospecting. Jour. Applied Ecology. 7:429. As cited in Versar (1979).

U.S. Dept. of Health, Education and Welfare (HEW). 1970. Community Water Supply Study. Public Health Service, Environmental Health Service, Bureau of Water Hygiene.

U.S. Environmental Protection Agency. 1977a. Information for proposed general pretreatment regulations (40 CFR 405), Washington, D.C.

U.S. Environmental Protection Agency. 1977b. The prevalence of subsurface migrations of hazardous chemical substances at selected industrial waste disposal sites.

U.S. Environmental Protection Agency. 1979a. Effluent guidelines and standards; electroplating point source category; pretreatment standards for existing sources. Federal Register 44(175):52590-52628.

U.S. Environmental Protection Agency. 1979b. Copper - ambient water quality criteria. Criteria and Standards Division, Office of Water Planning and Standards.

U.S. Environmental Protection Agency. 1979c. STORET.

Versar, Inc. 1979a. Copper statement of probable fate. Draft report to Monitoring and Data Support Division, U.S. Environmental Protection Agency.

Versar, Inc. 1979b. Non-aquatic fate of copper. Draft report to Monitoring and Data Support Division, U.S. Environmental Protection Agency.

Vuceta, J. and J.J. Morgan. 1978. Chemical modeling of trace metals in fresh waters: Role of complexation and adsorption. Environ. Sci. Technol. 12(12):1302-1308.

Weast, R.C. (Ed.). 1972. Handbook of Chemistry and Physics, 53rd Edition. The Chemical Rubber Co., Cleveland, OH.

Whaling, P.J., R.T. Barber, and J.C. Paul. 1977. The distribution of toxic metals in marine ecosystems as a result of sewage disposal and natural processes. Water Resources Research Institute of the University of North Carolina (NTIS PB-277 644).

Wright, E.M. and J.M. Diamond. 1968. Effects of pH and polyvalent cations on the selective permeability of gall-bladder epithelium to monovalent ions. Biochem. Biophys. Act 168:57-74. As cited in Mierle & Stokes (1976).

Yopp, J.H., W.E. Schmid, and R.W. Holst. 1974. Determination of maximum permissible levels of selected chemicals that exert toxic effects on plants of economic importance in Illinois. Report to Illinois Institute for Environmental Quality.

Yost, K.J. and A. Scarfi. 1979. Factors affecting copper solubility in electroplating waste. J. Water Pollution Control Fed. 51(7):1887-1896.

Yost, K.J. and D.R. Masarik. 1977. A study of chemical destruct waste treatment systems in the electroplating industry. Plating and Surface Finishing, January:35-40.

SECTION V.

EFFECTS OF AND EXPOSURE TO COPPER - AQUATIC ORGANISMS

A. EFFECTS OF COPPER

1. Introduction

This section provides information about the levels of copper exposure at which the normal behavior and metabolic processes of aquatic organisms are disrupted, as indicated by laboratory and field studies. Copper is a contaminant for which a considerable amount of data on effects are available, and the opportunity exists to investigate the biological and chemical aspects of toxicity more thoroughly than with most other priority pollutants.

While such data have provided a better understanding of copper toxicity, they have also illustrated the complexity of the interactions between copper and the aquatic environment. Laboratory experiments that attempt to isolate the effects of a single variable on copper toxicity may fail to account for other parameters that are known to modify substantially the availability of copper to an organism. For example, copper complexes with a wide variety of organic compounds, which effectively reduce its toxicity. Yet levels of organic complexing agents are seldom measured or reported in field studies. Other metals in the water, such as zinc or lead, may act synergistically or antagonistically with copper to increase or decrease its toxicity. Since the toxicant solutions used in laboratory studies usually have negligible concentrations of either organic complexing agents or other heavy metals, the resulting data are inaccurate to the extent that they cannot be extrapolated to field situations where these other factors are significant. On the other hand, so many variables exist in field experiments that the results are difficult to generalize to other areas or conditions.

Most toxicity studies do measure such parameters as pH and hardness, which are important in that they determine the degree and nature of copper complexation. Certain complexes have been identified that are apparently more toxic than others. The cupric ion is the most prevalent form of copper at lower pH values (6 or less) and is also thought to be the most toxic. Unfortunately, few bioassays are conducted in midly acidic water in order to test this assumption.

As a result of the many variables that influence the results of copper toxicity bioassays, the data discussed below can provide only a rough estimate of copper concentrations that can be expected to have adverse effects on aquatic life. The implications of these variables will be discussed further in the consideration of risk (Section VII).

Preceding page blank

2. Freshwater Organisms

a. Chronic/Sublethal Toxicity

Copper is an essential micronutrient for biota, but there is a fine line between the concentrations at which it is beneficial and the levels at which it becomes toxic. Low concentrations of copper can cause a wide variety of reactions in aquatic organisms, ranging from behavioral changes to growth inhibition and physical deformity. Although copper in small quantities (e.g., less than 20 μg/L) may not be fatal to fish, it can pose a threat to the species as it has been shown to diminish reproductive potential in the laboratory.

Folmar [1976, as cited in Tracor Jitco, Inc. (TJI, 1977)] has observed an avoidance reaction to concentrations of 0.1 μg/L copper (hardness, 89.5 mg/L) by the rainbow trout (*Salmo gairdneri*), while Sprague *et al.* (1965, as cited in TJI, 1977) have reported a similar response by Atlantic salmon (*Salmo salar*) to 2.4 μg/L copper (hardness, 20 mg/L). Sublethal effects on freshwater fish have been reported for concentrations ranging from 9 μg/L to 1000 μg/L. Physiologic effects include accumulation of mucous on the gills (resulting in a "cough" response), changes in gill ATPase activity and olfactory response, and a loss of ability to regulate water balance. These concentrations of copper can alter behavior, as well as inhibit reproduction, migration, and growth. Data on sublethal effects are outlined in Table 15.

Data on the sublethal effects of copper on freshwater invertebrates are much more limited, and can be summarized as follows. Cheng and Sullivan (1977) tested the osmoregulatory effects of copper sulfate in the snail (*Biomphalaria glabrata*), and found that concentrations as low as 60 μg/L caused a large influx of water into the tissues, resulting in death with 12 to 48 hours. A copper sulfate concentration of 14.8 μg/L inhibited growth in the snail (*Physa integra*) and the scud (*Gammarus Pseudolimneus*), and suppressed feeding in the snail (*Campelona decisum*) (Arthur and Leonard, 1970).

Chronic toxicity of copper has been examined by several investigators Sauter *et al.* (1976) have reported a 60-day chronic exposure to 5 μg/L, which reduced the growth of brook trout (*Salvelinus fontinalis*) embryos and larvae in soft water. In other 60-day tests, chronic values of less than 40 μg/L copper have been reported for the rainbow trout (*Salmo gairdneri*) and white sucker (*Catostomus commersoni*) in soft water (~45 mg/L $CaCO_3$ hardness) (McKim *et al.*, 1978). Effects due to chronic exposure have been observed for catfish (*Ictaulurus punctatus*) at concentrations of less than 20 μg/L copper in soft water (32 to 51 mg/L hardness). Chronic values for the snail and scud and other invertebrate species range from 6.1 μg/L to 49.0 μg/L.

TABLE 15. SUBLETHAL EFFECTS OF COPPER ON FRESHWATER FISH

Copper Conc. (µg/L	Species	Compound	Hardness (mg/L)	pH/Temp (°C)	Test Duration	Test Type	Effects	Reference
0.1	Rainbow Trout (Salmo gairdneri)	$CuSO_4$	89.5	8.0/-	1 hr	flow-thru	Avoidance behavior	Folmar (1976) as cited in TJI (1977)
2.4	Atlantic Salmon (Salmo salar)	$CuSO_4$	20	-/15-17°	-	flow-thru	Avoidance behavior	Sprague et al. (1965), as cited in TJI (1977)
5	Coho Salmon (Oncorhynchus kisutch)	$CuCl_2$	89-99	6.8-7.9/12°	1 mo	field	Reduced downstream migration	Lorz and McPherson (1976)
		followed by field test						
9	Brook Trout (Salvelinus fontinalis)	$CuSO_4$	45	7.65/8.5°	48 hr	flow-thru, nominal	Significant increase in cough response, increased activity, less aggressive feeding	Drummond et al. (1973), as cited in TJI (1977)
18.4	Fathead Minnow (Pimephales promelas)	$CuSO_4$	31	7.1/19-25°	11 mo	flow-thru measured	LC_{50}; prevented spawning, retarded growth & sex development of survivors	Mount and Stephan (1969)
20	Coho Salmon (Oncorhynchus kisutch)	$CuCl_2$	89-99	6.8-7.1/12°	1 mo	field	Decrease in gill ATPase activity	Lorz and McPherson (1976)
		followed by field test			1 mo		Decreased survival in seawater	
20	Rainbow Trout (Salmo gairdneri)	$CuSO_4$	90	7.7/13.0°	10 sec per 2 min.	perfusion of olfactory organs, measured	Threshold reduction in olfactory bulbar response to L-serine	Hara et al. (1976)

TABLE 15. SUBLETHAL EFFECTS OF COPPER ON FRESHWATER FISH (continued)

Conc µg/L	Species	Compound	Hardness (mg/L)	pH/Temp (°C)	Test Duration	Test Type	Effects	Reference
27	Brown Bullhead (Ictalurus nebulosus)	$CuSO_4$	202	7.6/varied	600 day	static, measured	Decr. in plasma glutamic oxaloacetic transaminase (PGOT)	McKim, et al (1970), as cited in TJI (1977)
32.5	Brook Trout (Salvelinus fontinalis) (yearlings)	$CuSO_4$	45.5	7.5/10.6°	8 mo	flow-thru, measured as dissolved Cu	Decreased survival slighly decreased growth	McKim and Benoit (1974)
36	Zebrafish (Brachydanio rerio) (eggs)	$CuSO_4$	16(alk.)	-/26°	-	static, measured	Suppressed hatching nervous system malformations	Ozch (1979)
70	Rainbow Trout (Salmo gairdneri)	$CuSO_4$	60	7.8/15°	48 hr	flow-thru, measured	Increased cough frequency	Sellers et al. (1975)
100	Rainbow Trout (Salmo gairdneri)	$CuSO_4$	365	-/10°	40 day	static	Initial depression of feeding and growth, followed by acclimation	Lett et al. (1976)
162	Bluegill Sunfish (Lepomis macrochirus) (juveniles)	$CuSO_4$	45	7-8/20-27°	22 mo	flow-thru, measured as total Cu	Reduced survival, inhibited spawning retarded growth	Benoit (1975)

TABLE 15. SUBLETHAL EFFECTS OF COPPER ON FRESHWATER FISH (continued)

Conc µg/l.	Species	Compound	Hardness (mg/l.)	pH/Temp (°C)	Test Duration	Test Type	Effects	Reference
1,000	Striped Bass (*Roccus saxatilis*) (juveniles)	$CuSO_4$		-17.5°	10 day acclimation 5 min exposure	-	Overall loss of ability to regulate water balance	Courtois (1976), as cited in TJI (1977)
	Sea-water acclimated		30				Lost weight, incr. serum Na	
	Fresh-water acclimated						Gained weight, decr. serum Na	
180	Fathead Minnow (*Pimephales promelas*)	$CuSO_4$	148-340	7.6-8.6/2-30°	9 mo.	static, nominal	Complete inhibition of spawning	Brungs *et al.* (1976)
1,000	Striped Bass (*Roccus saxatilis*)	$CuSO_4$	-	-/19.0°	15 min	static, nominal	Expansion of plasma volume	Courtois and Meyerhoff (1975)

b. Acute Toxicity

Acute toxicity is defined as toxicant-induced mortality over a short period, generally within 96 hrs. Although fish are more likely to be exposed to concentrations resulting in chronic or sublethal effects, run-off from a tailings dump or an industrial discharge can temporarily result in levels high enough to cause fish kills.

The acute effects of copper have been extensively studied for a wide variety of freshwater fish. LC_{50} values for 24- to 96-hr exposures varied from 10 µg/L for Chinook salmon (Oncorhynchus tshawytscha) (hardness = 13 mg/L) to more than 10,000 µg/L (hardness = 200 mg/L) for the bluegill sunfish (Lepomis macrochirus). In addition to all salmonid species, the fathead minnow (Pimephales promelas) appears to be more susceptible to low concentrations of copper than other freshwater species tested.

The available data are outlined in EPA (1979), and have been condensed in Table 16. While it is apparent that toxicity is to some degree species-dependent, there are numerous other factors contributing to variability that will be discussed in Part 5 of this section.

LC_{50} values for freshwater invertebrates range over several orders of magnitude, from 5 µg/L (hardness of 66 mg/L $CACO_3$) for Daphnia hyalina to 9,300 µg/L (hardness of 50 mg/L $CACO_3$) for snail (Amnicola lycorias). Other particularly sensitive species include the scud (Gammarus pseudolimnaeus) and the midge (Chironomous sp.), with 96-hours LC_{50} values of 20 µg/L and 30 µg/L, respectively. For a complete summary of existing data, the reader is referred to Table 2 in U.S. EPA (1979).

Copper concentrations from 1 µg/L to 8,000 µg/L have been shown to inhibit the growth or photosynthesis of various freshwater plant species. Among the most susceptible are the alga species Chlorella pyrenoidosa and C. regularis, and the diatom, Nitzschia palea. Other data on freshwater plants are listed in Table 5 in U.S. EPA (1979).

3. Marine Organisms

Relatively little research has been conducted on the toxicity of copper to marine vertebrates. EPA (1979) contained no information on chronic or sublethal effects in their review. Birdsong et al. (1971, as cited in EPA, 1979) found 96-hr LC_{50} values of 360, 380 and 410 µg/L for the Florida pompano (Trachinotus carolinus). Embryos of the summer flounder (Paralichthys dentatus) were found to be more susceptible, with median lethality occurring after 96 hours of exposure to 38 µg/L (Cardin et al., 1978, as cited in U.S. EPA, 1979).

In tests of copper toxicity for saltwater invertebrates, the clam (Venerupis decussata) was among the most sensitive organisms, exhibiting reduced burrowing activity and increased mortality at a copper concentration of 10 µg/L over a 90-day exposure period. (Stephenson and Taylor, 1975). Saliba and Krzyz (1976) observed a decrease in the growth rate of the brine shrimp (Artemia salina) at a concentration of 10 µg/L copper

TABLE 16. ACUTE TOXICITIES OF COPPER FOR FRESHWATER FISH[1]

Total Copper Concentration (μg/L)	Species	Hardness (mg/L) as $CaCO_3$
10- 190	Chinook Salmon (*Oncorhynchus tshawytscha*)	13- 182
15.7[2]- 367[2]	Cutthroat Salmon (*Salmo clarki*)	18- 205
17- 1,100	Rainbow Trout (*Salmo gairdneri*)	21- 371
23- 2,336	Fathead Minnow (*Pimephales promelas*)	20- 360
32- 125	Atlantic Salmon (*Salmo salar*)	8- 20
36- 1,250	Guppy (*Poecilia reticulata*)	20-87.5
36- 2,900	Goldfish (*Carassius auratus*)	20- 40
43- 780	Coho Salmon (*Oncorhynchus kisutch*)	20- 99
50- 4,300	Striped Bass (*Morone saxatilis*)	53-68.4
100	Brook Trout (*Salvelinus fontinalis*)	45
150- 620[2]	Bluntnose Minnow (*Pimephales notatus*)	194- 324
180- 570[2]	Brown Bullhead (*Ictalurus nebulosus*)	200- 303
230- 330	Golden Shiner (*Notemigonius chrysoleucas*)	36
290- 340[2]	Stoneroller (*Campostoma anomalum*)	200- 318
310- 1,050[2]	Creek Chub (*Semotilus atromaculatus*)	200- 316
320	Blacknose Dace (*Rhinichthys atratulus*)	200
320- 630[2]	Rainbow Darter (*Etheostoma caeruleum*)	200- 318
350- 375	Flagfish (*Jordanella floridae*)	1,270

---

[1] Taken from Table 1, U.S. EPA (1979)

[2] Dissolved copper

[3] Rao *et al.* (1975) as cited in TJI (1977)

TABLE 16. ACUTE TOXICITIES OF COPPER FOR FRESHWATER FISH (Continued)

Total Copper Concentration (µg/L)	Species	Hardness (mg/L) as $CaCO_3$
425[3]- 810	Carp (*Cyprinus carpio*)	53- 55
590[2]- 850	Orangethroat Darter (*Etheostoma spectabile*)	200- 318
610	Johnny Darter (*Etheostoma nigrum*)	316
630[2]- 1,900	Striped Shiner (*Notropis chrysocephalus*)	200- 318
660-10,200	Bluegill Sunfish (*Lepomis macrochirus*)	20- 318
840- 860	Banded Killifish (*Fundulus diaphanous*)	53- 55
1,432	Rock Bass (*Ambloplites rupestris*)	24
2,400- 2,700	Pumpkinseed (*Lepomis gibbosus*)	53- 55
2,600- 3,700	Channel Catfish (*Ictalurus punctatus*)	36
6,000- 6,400	American Eel (*Anguilla rostrata*)	53- 55
6,200- 6,400	White Perch (*Morone americanus*)	53- 55

---

[1] Taken from Table 1, U.S. EPA (1979)
[2] Dissolved copper
[3] Rao *et al.* (1975), as cited in TJI (1977)

over 13 days. Behavior and development in the coral (Echinometra mathaei) were adversely affected at 20, 30, and 50 μg/L in a study by Heslinga (1976, as cited in TJI, 1977). Other chronic and sublethal effects are described in Table 17.

According to the data compiled in U.S. EPA (1979), the LC_{50} values for marine invertebrates ranged from 9 μg/L for the calanoid copepod (Acartia tonsa) (Sosnowski and Gentile, 1978, as cited in U.S. EPA, 1979), to 600 μg/L for shore crab (Carcinus maenas) larvae (Connor, 1972, as cited in U.S. EPA, 1979). Other particularly sensitive species include American lobster (Homarus americanus) larvae with median lethality at 48 μg/L (Johnson and Gentile, 1979), and the soft-shelled clam (Mya arenaria) with a 96-hr LC_{50} of 39 μg/L. The available data are summarized in Table 9 in U.S. EPA (1979).

Most of the marine plants tested for copper toxicity were microalgae, which responded to high copper levels with decreased rates of growth and photosynthesis. U.S. EPA (1979) refers to the EC_{50} value for plants, which is the effective concentration at which photosynthesis or growth is inhibited by 50%. The lowest EC_{50} value reported was 5 μg/L, for the alga species Thalassiorsiria pseudonana (Erikson, 1972, as cited in U.S. EPA, 1979) and Scripsiella faeroense (Saifullah, 1978, as cited in U.S. EPA, 1979). A study of copper toxicity to 18 species of marine algae by Berland et al. (1976, as cited in TJI, 1977) indicated that dinoflagellates are more sensitive as a group than diatoms. Other marine algae data are listed in Table 11 in U.S. EPA (1979).

4. Other Studies

In order to understand the effects of low copper concentrations on a natural ecosystem, a series of experiments was conducted under controlled field conditions in marine waters in British Columbia. A description of the system used can be found in Menzel and Case (1977). These CEPEX (controlled ecosystem pollutant experiment) investigations focused on population responses to copper as reflected by changes in biomass productivity, activity, taxonomic diversity and other parameters. Table 18 describes the responses of various species groups as reported by five different studies. The results indicated that aqueous copper concentrations between 5 μg/L and 50 μg/L had a measurable impact on the biotic communities and that the responses varied by species. Moreover, the copper-sensitive species were commonly replaced by more tolerant species.

5. Factors Affecting the Toxicity of Copper

Numerous variables in a natural aquatic environment may strongly influence the availability and toxicity of copper to biota. Various chelating, complexing, and precipitating agents may bind with copper so that it is made unavailable for uptake. The hardness, alkalinity, and salinity of the water affect copper toxicity because of (alkali and alkaline metal-copper) antagonism and carbonate complexing. In addition, other water parameters such as temperature pH, and other heavy metal concentrations may modify the effects of copper.

TABLE 17. CHRONIC/SUBLETHAL EFFECTS OF COPPER ON MARINE INVERTEBRATES

Conc. µg/L	Species	Compound	Salinity ppt	pH Temp (°C)	Test Duration	Test Type	Effects	Reference
10	Clam (*Venerupis decussata*)	$CuSO_4$	~30	-/15^{o}	90 day	Static	Mortality; reduced burrowing activity	Stephenson and Taylor (1975)
10	Brine Shrimp (*Artemia salina*)	$CuSO_4$ and $Cu(CH_2COOH)_2$	37.5	-/21-22^{o}	13 day	Static	Decrease in growth rate	Saliba and Krzyz (1976)
20	Coral (*Echinometra mathaei*)	$CuCl_2$	32.6-35.0	8.2-8.5/28^{o}	42 hr	Static, Nominal	Irregular, retarded growth	Heslinga (1975), as cited in TJI (1977)
30	"	"	"	"	24 hr	"	Loss of righting response, adherence to wall, and response to light	"
50	"	"	"	"	10 mn	"	25% decrease in fertilization	"
>100	Mud Snail (*Nassarius obsoletus*)	$CuCl_2$	25	-/20^{o}	72 hr	Static, Measured as dissolved Cu	50-75% decrease in oxygen consumption	MacInnes and Thurnberg (1973) as cited in TJI (1977)
300	Mussel (*Mytilus edulis*)	$CuCl_2$	~30	8.0-8.2/10^{o}	15 hr	Static	Decreased respiration	Scott and Major (1952), as cited in TJI (1977)
300	"				1 hr		Decreased heartbeat rate	"
5,000	Barnacle (*Balanus crenatus*) (Larvae)	$CuSO_4$	33	-/-	15 mn	Static	Larvae unable to settle	Pyefinch and Mott (1948), as cited in TJI (1977)

TABLE 18 REPORTED RESULTS FROM CEPEX STUDIES

Copper µg/L	Species	Response	Source
5, 10, 50	Zooplankton	No definable effect (>80% reduction on z.p. abundance in both control and copper treated system)	Gibson and Grice (1977)
5, 10, 50	Ctenophores and medusae	Lower numbers than in control	Gibson and Grice (1977)
5, 10	Copepods (*pseudocalanus*, *Calanus*, *Euphasia*, and *Pleurobrachia*)	Reduced activity and reduction in egg and fecal pellet production	Reeve *et al.*(1977)
10, 50	Bacteria (heterotrophs)	Increase in numbers and activity due to release of available organic carbon from copper-sensitive species	Vaccaro *et al.* (1977)
5, 10, 50	Algae	Change in species composition; replacement of sensitive species with more resistent species	Thomas and Seibert (1977)
5, 10, 50	Phytoplankton	Initial inhibition of growth until replacement by resistant species	Harrison *et al.* (1977)

Of all the uncertainties surrounding the validity of copper toxicity bioassays, the complexity of the chemistry of aqueous copper is perhaps the most significant. Many substances, both organic and inorganic, may bind with copper (see Chapter IV) and perhaps render it inactive as a toxicant (Brown, 1968). Chelating agents such as pyrophosphate are particularly effective in this respect (Manahan, 1972). Many such compounds are synthetic in origin and may be found as pollutants in water bodies; their presence can actually mitigate the toxic effects of copper. Zitco et al. (1973) found that the incipient lethal level of copper for Atlantic salmon (Salmo salar) was increased from 25 µg/L to 110 µg/L with the addition of 10 µg/L humic acid to the test medium, and to 240 µg/L with the addition of 10 µg/L fulvic acid. Sprague (1968) also observed mitigative effects for brook trout (Salvelinus fontinalis) using nitrilotriacetic acid (NTA); survival in a solution of 50 µg/L copper was prolonged from 10 hr to 47 hr with the addition of 50 µg/L NTA. Similarly, when Shaw and Brown (1974) added NTA to copper sulfate solutions, the LC_{50} for rainbow trout (Salmo gairdneri) increased from 140 µg/L to 500 µg/L. In a copper toxicity test with the clam (Venerupis decussata), Stephenson and Taylor (1975) added excess (1.0 µg/L) ethylenediaminetetra acetic acid (EDTA) to a solution of 100 µg/L copper. Clams in 100 µg/L copper solution alone did not survive beyond 50 days, while those in 100 µg/L copper and 1.0 mg/L EDTA exhibited no signs of toxicosis.

Geckler et al. (1976) added copper directly and continually to a stream, and the toxicity of the contaminated stream water was tested in bioassays with a number of warm water species. These authors found that copper was much less toxic in this stream water than would have been predicted based on its hardness (330 mg/L $CaCO_3$) and that the toxicity of copper in this stream water varied over a 5-month period. For rainbow darter, a 24-hr LC_{50} ranged from less than 4.9 mg/L to 18 mg/L copper. The study concluded that the variable toxicity of copper in this stream was due to the effluents of an upstream sewage treatment plant; presumably the organic constituents were forming copper complexes, thus reducing toxicity.

Organic ligands apparently detoxify the cupric ion by occupying one or both valences so that the copper loses its ability to be absorbed or metabolized. However, the effect of inorganic complexing, particularly with carbonates, on copper toxicity is not as well understood. Shaw and Brown (1974) reported that copper toxicity is related to the cupric ion and aqueous copper carbonate together. Andrew et al. (1977) found that toxicity is related only to the cupric ion, and stated that Shaw and Brown's interpretation does not account for differences observed in waters of widely differing alkalinity. Howarth and Sprague (1978, as cited in Chakoumakos et al., 1979) concluded that $CuOH^+$ and $CU_2(OH)^{++}$ are also toxic, in addition to the cupric ion.

In any event, the inverse relationship between water hardness (and calcium-associated alkalinity) and copper toxicity is a well-documented phenomenon, which essentially has two aspects. Inorganic complexing in the form of carbonates and hydroxides, which reduces the concentration of free cupric ion, is maximized in hard alkaline water. Conversely, a low pH and soft water reduce carbonate complexing and increase the proporation of free ionic copper. The other factor apparently affecting toxicity is calcium concentration, which is also related to water hardness.

Hard water has high concentrations of calcium, which competes with copper for absorption and metabolism in biota and thus effectively reduces copper toxicity. Although this interaction is largely hypothetical, it has been implicated for other heavy metals such as zinc (Matthiesson and Brafield, 1977).

In seawater, copper decreases in solubility as it mixes with relatively high concentrations of sodium, calcium, magnesium, and other light metals (U.S. EPA, 1979). However, copper adsorbed onto particles tends to be released in estuarine conditions. (See Environmental Fate, Chapter IV.) The only study found in which the effects of salinity on copper toxicity were tested was by Jones *et al*. (1976, as cited by TJI, 1977), using the polychaete *Nereis diversicolor*. They found that resistance to copper was least at 5 ppt and 34 ppt salinity (the lowest and highest salinities used).

Studies by Smith and Heath (1979) and Rehwoldt *et al*. (1972) on a total of seven species of freshwater fish indicate that temperature variations between 5° and 30°C have no significant effect on copper toxicity.

The presence of other chemicals may also influence the effects of copper on aquatic organisms. Calamari and Marchetti (1973) tested the effects of ionic and nonionic surfactants on the toxicity of copper to rainbow trout. The two ionic surfactants (sodium alkylbenzene sulfonate and sodium laurylbenzene sulfonate) acted synergistically with copper so that the toxicity was increased. Andrew *et al*. (1977) found that the inorganic chelating agent pyrophosphate increased copper perchlorate solubility, but actually decreased its toxicity to *Daphnia magna*. Orthophosphate decreased both solubility and toxicity.

In waters that are polluted with copper from mining or industrial activities, other heavy metals are often found as well. Lead, mercury, cadmium, and zinc are all toxic to varying degrees, and have some similar effects on aquatic life. The interaction of two heavy metals was studied by Ozoh and Jacobson (1979), who exposed zebra ciclid (*Cichlasoma nigrofasiciatum*) eggs to concentrations of 0, 16, and 32 μg/L of copper and zinc, alone and in combinations. They found that the synergy of copper and zinc interfered more with hatching and normal growth than comparable concentrations of a single metal. Lorz *et al*. (1978) observed that coho salmon (*Oncorhynchus kisutch*) exposed to copper (10 μg/L) or copper:zinc (10:400 μg/L) solutions did not feed as well as when exposed to zinc (400 μg/L) alone.

The interactions between heavy metals are not always synergistic, however. A study by Roales and Perlmutter (1974) provides evidence of mutual suppression by methylmercury ($HgCH_3$) and copper when combined in solution. At low to moderate concentrations of copper (20-90 μg/L), the blue gourami (*Trichogaster trichopterus*) experienced lower mortality when methylmercury was added. Similarly, Ozoh (1979) found that the presence of lead ions reduced the hatching inhibition and abnormal development effects of copper in the zebrafish (*Brachydanio rerio*).

Although only the toxic effects of copper have been described in this section, in some cases copper at low concentrations can be beneficial to aquatic life, aside from its role as a micronutrient. Ozoh and Jacobson (1979) observed greater hatching success in zebra ciclid eggs in 16 μg/L copper than in lower concentrations. They attributed the lower mortality to the fungicidal and bactericidal effects of the copper ions.

6. Conclusions

According to the literature surveyed, the lowest concentration of copper at which adverse effects have been observed in an aquatic organism is 1 μg/L, which caused a growth lag in the freshwater alga, Chlorella pyrenoidosa. (It should be noted that 1 μg/L or higher is the background level of copper in many areas.) The lowest "chronic value" reported is 5 μg/L, for the brook trout (Salvelinus fontinalis) in soft water. Acute effects appeared with exposure to 10 μg/L for the Chinook salmon (Oncorhynchus kisutch). The salmonids as a group are the most sensitive freshwater fish, in addition to the fathead minnow (Pimephales promelas). Daphnia hyalina was the most sensitive of the freshwater invertebrates tested, with a 96-hr LC_{50} of 5 μg/L. Other sensitive species are the scud (Gammarus pseudolimnaeus), with a chronic value of 6.1 μg/L, and the midge (Chironomous sp). Thus the concentration at which acute and chronic effects may occur for a variety of freshwater species is 10 μg/L or less, according to the laboratory studies surveyed.

Marine toxicity data were limited, and the lowest reported LC_{50} concentration was 28 μg/L for summer flounder (Paralichthys dentatus) larvae. Among invertebrates, the clam (Venerupis decussata) was the least resistant to copper, with adverse effects reported at 10 μg/L. The calanoid copepod (Acartia tonsa) and the soft-shelled clam (Mya arenaria) are also comparatively sensitive to copper. The lowest EC_{50} value recorded was 5 μg/L, for the alga (Thalassiosira pseudonana).

An overview of the data suggests that in many cases the stage of the life cycle is an important factor in a species resistance to copper. Generally speaking, adults and eggs were less susceptible to copper than larvae and juveniles.

The toxicity of copper is strongly influenced by a number of environmental factors. Complexing, chelating, and precipitating agents, both organic and inorganic, generally decrease the toxicity of copper by bonding, which renders it unavailable for metabolism. In general, however, copper toxicity (particularly of inorganic complexes) increases as water pH and hardness decrease.

Other heavy metals often occur with copper, which hinders further any efforts to isolate the effects of an individual parameter. Laboratory studies indicate that zinc and copper are synergistic, while lead and methyl mercury are antagonistic to copper toxicosis.

In summary, general concentration ranges can be established at which certain effects are seen in the laboratory. However, these ranges are not rigidly defined, and may overlap as a result of differences among species or environmental variables.

- <5 μg/L This represents the detection limit for some copper measurements. Few adverse effects have been observed at this level even in the softest water (some algae are exceptions).
- 6-20 μg/L Sublethal effects as a result of an acute or chronic exposure have been reported for sensitive species at the upper end of this range and in very soft water. Lethal effects have been reported for sensitive salt- and freshwater invertebrates (the latter in very soft water) and for some algae.
- 20-60 μg/L This range is reported as chronically and acutely toxic for a wide range of species in very soft water; sublethal effects for many species have been reported for this range in soft and moderately hard water (200 mg/L $CaCO_3$).
- 60-120 μg/L Some lethal effects for sensitive species have been reported in moderately hard and hard water in this range, and less sensitive species show effects in soft water (vertebrate and invertebrate); sublethal effects for less sensitive species have also been observed in this range.
- 120-300 μg/L Only the most tolerant species tested in hard water can consistently survive these concentrations. However, LC_{50} values have been reported as high as 10,000 μg/L
- >300 μg/L Values in this range reported toxic to a large variety of species in all but the hardest water.

B. EXPOSURE OF BIOTA TO COPPER

1. Introduction

Copper is a relatively abundant metal in the earth's crust, and occurs naturally in small concentrations in most fresh and saltwater bodies. Levels of copper in undisturbed environments are determined largely by the composition of the local substrate, which varies geographically.

Human activities such as mining and manufacturing have substantially increased the amount of free copper in the environment by removal from ore and through emissions in various forms (see Section III). Copper is also intentionally distributed through its use in agriculture and as an algicide. New York City maintains a .059 μg/L copper concentration in its reservoirs for its algicidal properties (NRC, 1977), although levels as high as 1 mg/L are commonly used elsewhere.

The toxic effects of copper are significantly modified by numerous factors, including pH, hardness, and the concentration of complexing agents or other heavy metals. While toxicity probably decreases with increasing salinity, copper adsorbed onto particulates in freshwater may be released upon contact with saltwater, e.g., in an estuary. These factors were discussed in Section IV.

2. Monitoring Data

The extensive data provided by STORET indicate that copper is a frequently measured parameter, and that significant concentrations are found in many regions of the U.S. In reviewing the data on minor river basins, only basins where ten or more copper samples had been taken were considered. Of the many variables that influence copper toxicity, only pH and hardness data were obtained, and so the effects of other factors cannot be assessed. Moreover, the STAND program (with which the data were retrieved) does not list individual station locations, and thus there is no indication of which pH and hardness measurements correspond to which copper measurement, except where data on individual stations were retrieved. Measurements of total copper (instead of dissolved copper) were used for the analysis because more monitoring data were available.

Table 19 shows that copper concentrations are high in certain minor river basins. Mean concentrations greater than 50 µg/L are found in areas of the Southeast and in the Ohio, Lower Mississippi, Gila, Spokane and Sacramento Rivers. For these areas, the majority of observed concentrations were less than 50 µg/L. Furthermore in many of these locations 10% or more of all observed concentrations exceeded 120 µg/L. This appears to indicate that a small number of high concentrations skew the mean concentration upward so that the calculated mean is not representative of typical concentrations found.

In order to examine this issue further, data were retrieved from the sampling stations in three minor basins with unusually high copper levels. Of the 125 copper measurements taken at various sampling stations along the Sacramento River in the California Basin, all of the high values were found at one station (Spring Creek below Debris Dam): all 17 samples taken at this station exceeded 1400 µg/L. Unfortunately, water hardness and pH were not measured at Spring Creek.

At eleven of the 24 sampling stations in the Gila River (Colorado River Basin), at least one copper measurement exceeded 250 µg/L, which could represent a harmful exposure level even in the hard water normally found in the area. At many stations, the hardness and copper measurements varied significantly during the sampling period (1978); these variations could be due to changes in discharge volume, seasonal stream flow, or other factors.

Among the 33 sampling stations in Zone 4 of the Delaware River (in the North Atlantic Basin), high copper levels were found primarily at Contrary Creek and in the Wilmington area. At the former station, more than 50% of 211 total copper measurements taken over a 15-month period were above 60 μg/L. Over 50% of the samples taken had a pH of less than 6, and the water was generally soft. However, the level of copper reported for an individual station ranged from 10 μg/L to 1,000 μg/L.

These data indicate that high concentrations of copper can be either localized (so that mean levels for an entire basin may be skewed by a few stations) or widespread. Assessing copper exposure in a specific area, therefore, required examining station data instead of relying on summaries of data for river basins.

3. Ingestion

No studies were found that described the uptake of copper by aquatic animals via ingestion. From the data discussed in Section IV, biomagnification through the food chain apparently does not occur, since tissues of higher level organisms do not have greater copper residues than those of lower-order biota.

4. Fish Kills

Table 20 provides information on the location and activities associated with fish kills attributed to copper between 1971 and 1977. Since many of the fish kills occurred in the presence of other metals and chemicals, it is not possible to isolate the effects of copper in the field. Moreover, the synergy between heavy metals may have increased the overall toxicity in many cases. Both game and non-game fish were affected by high levels of copper and other chemicals. No single industry was responsible for the majority of the reported discharges, and the kill events were distributed fairly evenly across the country.

In addition to the fish kills shown in Table 20, numerous fish kills have occurred as a result of copper sulfate use as an algicide. Though some of these appear to have resulted from misapplication, the circumstances of many incidents are unknown.

5. Conclusion

Because of the chemistry of aqueous copper and the nature and volume of data examined, it is difficult to draw firm conclusions about exposure levels, either on a regional or local level. Exposure levels are of concern where soft water, low pH, or higher copper levels (or a combination of these) occur. Such exposure may be seasonally variable, or related to point or non-point sources. As previously discussed, monitoring data can only be used to assess exposure potential rather than actual exposure, as information on the concentrations of organic and inorganic ligands is often lacking.

TABLE 19. COPPER OBSERVATIONS IN U.S. MINOR RIVER BASINS - 1978

River Basin Major/Minor	Name	Mean Cu >50 µg/L	≥50% of Cu >60 µg/L	≥10% of Cu >120 µg/L	≥50% of Hardness Measurements <50 mg/L
2/3	Delaware R. - Zone 1	*	*		
2/5	Delaware R. - Schuylkill	*	*		
2/6	Delaware R. - Zone 2	*			
2/7	Delaware R. - Zone 3	*	*		
2/8	Delaware R. - Zone 4	*	*	*	
3/7	Yadkin & Pee Dee Rivers	*			*
3/8	Catawba - Wateref, etc. Res.	*	*		*
3/9	Edisto - Combahef R.	*	*		*
3/13	Savannah R.	*	*		*
3/31[1]	Apalachicola R.			*	
3/32	Choctawhatchee R.			*	*
3/43	Pearl R.			*	*
4/3	French Broad R.			*	*
4/7	Duck R.	*		*	
4/8	Tennessee R.	*			
5/9	Big Sandy R.	*			
5/18	East Fork, White R.			*	
5/21	Ohio R.	*	*		
6/4	L. Erie Shore, Maumee R. to Sandusky R.	*			*
7/2	Hudson Bay, Rainy River	*			
7/13	Chicago Calumet R. - Des Plaines R.	*			
9/12	Lower Missouri R. from Niobrara R.	*			
10/11	Lower Mississippi R. - Yazoo R.			*	*
10/16	Lower Red R. — below Denison	*		*	
10/19	Atchafalaya R.	*	*	*	
10/20	Calcasieu R.	*			*
10/21	Lower Mississippi R.	*			
11/4	Gila R.	*		*	
12/1	Sabine R.	*		*	*
12/2	Neches R.	*	*	*	*
13/2	Clark Fork - Pend Oreille R.	*		*	
13/3	Spokane R.	*			*
14/4[1]	Central CA Coastal			*	
14/5[1]	Santa Clara R.	*	*		
14/9	Sacramento R.	*		*	*
15/7	Great Salt Lake	*			

---

[1] Fewer than 10 measurements at this station.

SOURCE: STORET

TABLE 20. DATA FOR COPPER-RELATED FISH KILLS, 1971-1977

Location	Source	Chemicals Implicated	Number of Fish Killed
Lake Hamilton, Arkansas	Metals production (general)	Cr, Zn, Cu, Ni, CN	14,940
Roaring Brook, Connecticut	Unreported	Phenol, Cu, Zn	300
Clark Fork River, Montana	Mining (power dam draw down)	Cu, Zn, Fe	?
Black River, Utah	Metals production (electroplating)	CN, Cu	2,000-3,000
Little Squaw Creek, Calif.	Mine tailings (abandoned)	Cu	59
Little Squaw Creek, Calif.	Mine tailings (abandoned)	Cu	10
Little Squaw Creek, Calif.	Mine tailings (abandoned)	Cu	100
Chadahem River, New York	Metals production (electroplating)	CN, Cu	25
Mill Creek, Washington	Cleaning Waste	Pb, Zn, Cu	100
Clinch River, Virginia	Power plant	Cu	6,000
Diablo Cove, California	Power plant (condenser tubes)	Cu	4,000
Housatonic Estuary, Conn.	Metals production	Ni, Cu, Zn	8,000
Pond to E. Providence reservoir, R.I.	Metals production	Cu, possibly Zn	?
Big Blue River, Indiana	Metals production (plating)	Cu, Ni, Cr	333
Tributary to M. Fork, Ellchorn Creek, Kentucky	Metals production	Cu, Zn	9,602

Source: Data files, Monitoring and Data Support Division, Office of Water Planning and Standards, U.S. Environmental Protection Agency

REFERENCES

Andrew, R.W., K.E. Biesinger, and G.E. Glass. 1977. Effects of inorganic complexing on the toxicity of copper to *Daphnia magna*. Water Research 11:309-315.

Arthur, J.W. and E.N. Leonard. 1970. Effects of copper on *Gammarus pseudolimnaeus*, *Physa integra*, and *Campeloma decisum* in soft water. J. Fish Res. Bd. Can. 27(7):1277-1283.

Bartlett, L.. and F.W. Rabe. 1974. Effects of copper, zinc, and cadmium on *Selenastrum capricornutum*. Water Research 8:179-185.

Benoit, D.A. 1975. Chronic effects of copper on survival, growth, and reproduction of the bluegill (*Lepomis macrochirus*). Trans. Amer. Fish Soc. 104(2):353-358.

Black, G.A.P., D.J. Hinton, C. Johnston, and J.B. Sprague. 1975. *Annotated List of Copper Concentrations Found Harmful to Aquatic Organisms*. Department of the Environment, Fisheries and Marine Service, Technical Report No. 603.

Brown, V.M. *et al*. 1974. Aspects of water quality and the toxicity of copper to rainbow trout. Water Research 8:797-803.

Brown, V.M. 1968. The calculation of the acute toxicity of mixtures of poisons to rainbow trout. Water Research 2:723-733.

Brungs, W.A., J.R. Geckler, and M. Gast. 1976. Acute and chronic toxicity of copper to the fathead minnow in a surface water of variable quality. Water Research 10:37-43.

Brungs, W.A., R.W. Carlson, W.B. Horning II, J.H. McCormick, R.L. Spehar, and J.D. Young. 1977. Effects of pollution on freshwater fish. J. Water Pollutant Control Fed. 49(b):1425-1493.

Bryan, G.W. 1976. Some aspects of heavy metal tolerance in aquatic organisms, In *Effects of Pollutants on Aquatic Organisms*, A.P.M. Lockwood (Ed.), Cambridge, Cambridge University Press.

Calamari, D. and R. Marchetti. 1973. The toxicity of mixtures of metals and surfactants to rainbow trout (*Salmo gairdneri* Rich.). Water Research 7:1453-1464.

Chakoumakos, C., R.C. Russo and R.V. Thurston. 1979. Toxicity of copper to cutthroat trout (*Salmo clarki*), under different conditions of alkalinity, pH, and hardness. Environ. Sci. Technol. 13(2):213-19.

Cheng, T.C. and J.T. Sullivan. 1977. Alterations in the osmoregulation of the pulmonate gastropod Biomphalaria glabrata due to copper. J. Invert. Pathol. 29(1):101-104.

Courtois, L.A. and R.D. Meyerhoff. 1975. Effects of copper exposure on water balance. Bull. Environ. Contam. Toxicol. 14(2):221-224.

Eisler, R. 1977. Acute toxicities of selected heavy metals to the softshell clam, Mya arenaria. Bull. Environ. Contam. Toxicol. 17(2): 137-144.

Gächter, R., K. Lum-Shue-Chan, and Y.K. Chau. 1973. Complexing capacity of the nutrient medium and its relation to inhibition of algal photosynthesis by copper. Schweiz, Z. Hyd. 35(2):252-261.

Geckler, R. W.B. Horning, T.M. Neiheisel, H. Pickering, E.L. Robinson and C.E. Stephan. 1976. Validity of Laboratory Test for Predicting Copper Toxicity in Streams. U.S. EPA, Environmental Research Laboratory-Duluth, Office of Research & Development.

Gibson, V.R. and G.R. Guice. 1977. Response of macro-zooplankton populations to copper: controlled ecosystem pollution experiment. Bull. Mar. Sci. 27:85-91.

Hara, T.J., Y.M.C. Law, and S. MacDonald. 1976. Effects of mercury and copper on the olfactory response in rainbow trout, Salmo gairdneri. J. Fish Res. Bd. Can. 33:1568-1573.

Harrison, W.G., R.W. Eppley, and E.H. Renger. 1977. Phytoplankton nitrogen metabolism, nitrogen budgets, and observations on copper toxicity: controlled ecosystem pollution experiment. Bull. Mar. Sci. 27(1):44-57.

Hartung, R. 1973. Biological effects of heavy metal pollutants in water. Adv. Exper. Med. Biol. 40:161-72.

Johnson, M.W. and J.H. Gentile. 1979. Acute toxicity of cadmium, copper, and mercury to larval American lobster Homarus americanus. Bull. Environ. Contam. Toxicol. 22:258-264.

Judy, R.D., Jr.. 1979. The acute toxicity of copper to Gammarus fasiatus say, a freshwater amphipod. Bull. Environ. Contam. Toxicol. 21:219-224

Kobot'yev, V.G., V.I. Kapkov, Ye.G. Ruishadze, N.V. Turunina, and N.A. Shidlovskaya. 1975. The toxic effect of copper complexes on algae. Gidrobiol. Zh. (Eng. transl.) 11(5):33-38.

Kleerekoper, H., G.F. Westlake, and J.H. Matis. 1972. Orientation of goldfish (Carassius auratus) in response to a shallow gradient of a sublethal concentration of copper in an open field. J. Fish. Res. Bd. Can. 29(1):45-54.

Lorz, H.W., R.H. Williams, and C.A. Fustich. 1978. Effects of Several Metals on Smolting of Coho Salmon. U.S. Environmental Protection Agency. Report No. EPA-60013-78-090.

Lorz, H.W. and B.P. McPherson. 1976. Effects of copper or zinc in fresh water on the adaptation to sea water and ATPase activity, and the effects of copper on migratory disposition of coho salmon (Oncorhynchus kisutch). J. Fish Res. Bd. Can. 33(9):2023-2030.

Lett, P.F., G.F. Farmer, and F.W.H. Beamish. 1976. Effect of copper on some aspects of the bioenergetics of rainbow trout (Salmo gairdneri). J. Fish. Res. Bd. Can. 33:1335-1342.

Manahan, S.E. 1972. Environmental Chemistry, Boston: Willard Grant Press.

Matthiesson, P., and A.E. Brafield. 1977. Uptake and loss of dissolved zinc by the stickleback Gasterostreus acuteatus L. J. Fish Biol. 10:399.

McKim, J.M., J.G. Eaton, and G.W. Holcombe. 1978. Metal toxicity to embryos and larvae of eight species of freshwater fish - II: copper. Bull. Environm. Contam. Toxicol. 19:608-16.

McKim, J.M. and D.A. Benoit. 1970. Effects of long-term exposures to copper on survival, growth, and reproduction of brook trout (Salvelinus fontinalis). J. Fish Res. Bd. Can. 28(5):655-62.

McKim, J.M. and D.A. Benoit. 1974. Duration of toxicity tests for establishing "no effect" concentrations for copper with brook trout (Salvelinus fontinalis). J. Fish. Res. Bd. Can. 31(4):448-451.

Menzel, D.W. and J. Case. 1977. Concept and design: controlled ecosystem experiment. Bull. Mar. Sci. 27:1-4.

Mount, D.I. and C.E. Stephan. 1969. Chronic toxicity of copper to the fathead minnow (Pimephales promelas) in soft water. J. Fish. Res. Bd. Can. 26(9):2449-57.

Okazaki, R.K. 1976. Copper toxicity in the pacific oyster Crassostrea gigas. Bull. Environm. Contam. Toxicol. 16(b):658-64.

Overnell, J. 1975. The effect of some heavy metal ions on photosynthesis in a freshwater alga. Pest. Biochem. Physiol. 5:19-26.

Ozoh, P.T.E. and C.O. Jacobson. 1979. Embryotoxicity and hatchability in Cichlasoma nigrofasciatum (guenther) eggs and larvae briefly exposed to low concentrations of zinc and copper ions. Bull. Environm. Contam. Toxicol. 21:782-86.

Ozoh, P.T.E. 1979. Malformations and inhibitory tendencies induced to Brachydanio rerio (Hamilton-Buchanan) eggs and larvae due to exposures in low concentrations of lead and copper ions. Bull. Environm. Contam. Toxicol. 21:668-675.

Raymont, J.E.G. and J. Shields. 1963. Toxicity of copper and chromium in the marine environment. Air Water Pollut. 7(415):435-443.

Reeve, M.R., J.C. Garnble, and M.A. Walter. 1977. Experimental observations on the effects of copper on copepods and other zooplankton: controlled ecosystem pollution experiment. Bull. Mar. Sci. 27(1):92-104.

Rehwold, R., L. Lasko, C. Shaw, and E. Wirhowski. 1973. The acute toxicity of some heavy metals ions toward benthic organisms. Bull. Environm. Contam. Toxicol. 10(5):291-94.

Rehwoldt, R., L.W. Menapace, B. Norric, and D. Alessandro. 1972. The effect of increased temperature upon the acute toxicology of some heavy metal ions. Bull. Environm. Contam. Toxicol. 8:91-95.

Roales, R.R. and A. Perlmutter. 1974. Toxicity of methylmercury and copper, applied singlely and jointly, to the blue gourami, Trichogaster trichopterus. Bull. Environm. Contam. Toxicol. 12(5):633-639.

Sauter, S., K.B. Buxton, K.J. Macek and S.R. Petrocelli. 1976. The Effects of Exposure to Heavy Metals on Selected Fresh Water Fish. Report to the U.S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research & Development, Duluth, Minnesota.

Saliba, L.J. and R.M. Krzyz. 1976. Acclimation and tolerance of Artemia salina to copper salts. Mar. Biol. 38:231-238.

Sellers, C.M., A.G. Heath, and M.L. Bass. The effect of sublethal concentrations of copper and zinc on ventilatory activity, blood oxygen and pH in rainbow trout (Salmo gairdneri). Water Research 9:401-408.

Shaw, T.L. and V.M. Brown. 1974. The toxicity of some forms of copper to rainbow trout. Water Research 8:377-82.

Smith, M.J. and A.G. Heath. 1979. Acute toxicity of copper, chromate, zinc, and cyanide to freshwater fish: effect of different temperatures. Bull. Environm. Contam. Toxicol. 22:113-119.

Solbé, J.F. de L.G., and V.A. Cooper. 1976. Studies on the toxicity of copper sulphate to stone loach Noemachilus barbatulus (L.) in hard water. Water Research 10:523-527.

Sprague, J.B. 1968. Promising anti-pollutant chelating agent NTA protects fish from copper and zinc. Nature (London) 220:1345-1346.

Stephenson, R.R. and D. Taylor. 1975. The influence of EDTA on the mortality and burrowing activity of the clam (Venerupid decussata) exposed to sub lethal concentrations of copper. Bull. Environm. Contam. Toxicol. 14(3):304-308.

Sugiura, K., S. Sato, and M. Goto. 1976. Toxicity assessment using an aquatic microcosm. Chemophere 2:113-118.

Sunda, W. and R.R.L. Guillard. 1976. The relationship between cupric ion activity and the toxicity of copper to phytoplankton. J. Mar. Res 34(4):511-529.

Thomas, W.H. and D.L.R. Seibert. 1977. Effects of copper on the dominance and the diversity of algae: controlled ecosystem pollution experiment. Bull. Mar. Sci. 27(1):23-33.

Tracor Jitco, Inc., TJI. 1977. Chapter VI. Environmental Fate and Effects: Copper. Draft report to Monitoring and Data Support Division, Office of Water Planning and Standards, U.S. Environmental Protection Agency.

U.S. Environmental Protection Agency. 1978. Reports of fish kills, 1971-1977. Data files, Monitoring and Data Support Division, Office of Water Planning and Standards.

U.S. Environmental Protection Agency (U.S. EPA). 1979. Ambient water quality criteria: copper. Criteria and Standards Division, Office of Water Planning and Standards.

Vaccaro, R.F., F. Azam, and R.E. Hodson. 1977. Response of natural marine bacterial populations to copper. Controlled ecosystem pollution experiment. Bull. Mar. Sci. 27:17-22.

Yopp , J.H., W.E. Schmid, and R.W. Holst. 1974. *Determination of Maximum Permissible Levels of Selected Chemicals that Exert Toxic Effects on Plants of Economic Importance in Illinois*. Report to Illinois Institute of Environmental Quality.

Zitco, P., W.V. Carson, and W.G. Carson. 1973. Prediction of incipient lethal levels of copper to juvenile Atlantic salmon in the presence of humic acid by cupric electrode. Bull. Environm. Contam. Toxicol. 10(5): 265-271.

VI. EFFECTS OF AND EXPOSURE TO COPPER--HUMANS

A. HUMAN TOXICITY

1. Introduction

Copper is an essential trace element in human and animal nutrition. The total body content of copper in a hypothetical 70-kg adult ranges between 100 mg and 150 mg (Ulmer, 1977). Liver, brain and kidney are rich in copper, but one-third of the body store of copper is in muscle tissue (Venugopal and Luckey, 1978).

As an essential component of key metalloenzymes, copper plays a vital role in numerous biochemical and physiological functions in higher animals. Most importantly, copper is involved in hematopoiesis, maintenance of vascular and skeletal integrity, and the structure and function of the central nervous system (O'Dell, 1976). Copper is also essential to iron utilization, is involved in the physiology of taste and smell, and functions in enzymes for energy production (Oster and Salgo, 1977; Venugopal and Luckey, 1978). Included among these cuproenzymes are cytochrome c oxidase, tyrosinase, ceruloplasmin, monoamine oxidase and dopamine β-hydroxylase (O'Dell, 1976).

a. Copper Deficiency

Animals deficient in copper exhibit anemia, vascular abnormalities, abnormal keratinization and depigmentation of hair, abnormalities in bone formation, myocardial fibrosis, demyelination of the central nervous system, gastrointestinal disorders, difficulties in parturition and neonatal ataxia (Vuori _et al_., 1978).

Newborn rats born to dams fed diets low in copper (0.5 mg/kg in the diet) were severely anemic and almost entirely non-viable. The copper-deficient-offspring showed a high incidence of skeletal anomalies and many had abdominal hernias; one-fourth of the offspring were affected with edema and a characteristic subcutaneous hemorrhage (O'Dell _et al_., 1961). Maternal copper deficiencies have also been shown to result in central nervous system abnormalities in lambs and guinea pig neonates (O'Dell _et al_., 1961).

Due to the relative abundance of copper in man's diet and its slow rate of excretion, the concept of copper deficiency in man was not widely accepted until recently. During the last decade, copper deficiency has been reported in small, premature infants (<1500 g) (al-Rashid and Spangler, 1971), in malnourished infants alimented exclusively by the intravenous route (Karpel and Peden, 1972), as well as in adults with malabsorption disorders (Dunlap _et al_., 1974). Serum copper and ceruloplasmin (the major plasma copper protein) drop and anemia, leukopenia and neutropenia often result (Ulmer, 1977; Graham and Cordano, 1976). Ceruloplasmin is believed to be necessary for the normal flow of iron from cells to plasma (Lee et al., 1976; Iwanska and Strusinska, 1978).

In humans, a sex-linked fatal disorder known as Menkes's syndrome results from a defect in the intestinal transport of copper. Affected male infants exhibit kinky, depigmented hair (due to defect in copper-linked disulfide bond formation), physical and mental retardation with widespread degeneration of the brain, and hypothermia; death generally occurs within the first few years of life (Ulmer, 1977; NRC, 1977).

There are other inherited metabolic diseases characterized by poor pigmentation and/or hair abnormalities suggesting that biochemical pathways involving copper enzymes are impaired. The metabolic defects in the varieties of albinism are in the pathways from tyrosine to melanin, and some forms of the disease involve differences in the copper enzyme tyrosinase (Oster and Salgo, 1977).

A more detailed discussion of the various manisfestations of copper deficiency in both man and animals may be found in Graham and Cordano (1976), NRC (1977), O'Dell et al. (1961), Oster and Salgo (1977), and Vuori et al. (1978).

2. Metabolism and Bioaccumulation

The average adult ingests between 2 mg and 5 mg of ionic copper daily (Ulmer, 1977). Approximately 30% of ingested copper is absorbed from the stomach, duodenum and jejunum; the unabsorbed copper is passed directly into the bowel. Effective net absorption, however, only about 5% due to excretion of copper into bile; biliary copper is bound to protein, and this complex is not reabsorbed (Frommer, 1977; Venugopal and Luckey, 1978). Copper absorption is influenced by a number of factors including its chemical form; the presence of competing ions such as zinc, iron, cadmium or molybdate in the diet; or the presence of certian amino acids and/or phytate (Venugopal and Luckey, 1978).

The absorption of copper salts from sites of parenteral injection is gradual, depending upon the solubility of salt. Absorption of copper-containing dusts via the lungs is similar. Absorption through the skin is minimal (Venugopal and Luckey, 1978).

Absorbed copper is present in serum as an exchangeable loose complex with serum albumin and as a firmly bound, copper metalloprotein, ceruloplasmin. The copper-albumin complex transports copper across membranes and distributes it to soft tissues. Ceruloplasmin formed in the liver, has a number of functions and appears to be a storage depot for copper. Ceruloplasmin accounts for 95% of the copper found in human plasma (Scheinberg and Steinlieb, 1960; Linder, 1977; Venugopal and Luckey, 1978).

Oral or intravenous administration of radiolabelled copper in humans is followed within 4 hrs by a transient rise in serum radioactivity that corresponds to the albumin fraction and is succeeded by a slower secondary rise corresponding to the release of newly synthesized ceruloplasmin from the liver (Adelstein and Vallee, 1961).

In mammals, the major excretory pathway of absorbed copper is via the bile (80%), with an additional 15% passed directly into the bowel. Small amounts are also excreted in urine (2-4%) and sweat (Adelstein and Vallee, 1961; Goodman and Gilman, 1975; Graham and Cordano, 1976). Human breast milk contains 10-70 µg/100 ml (Spector, 1956).

An efficient homeostatic mechanism for copper exists in man. In addition to the liver, the primary organ regulating copper metabolism, the intestinal mucosa, acts as a regulatory barrier to the absorption of excessive copper and for the release of copper into intestinal fluids (Venugopal and Luckey, 1978).

Mean concentraions of copper in serum of healthy men and women are in the 80-150 µg/100 ml range (Cartwright and Wintrobe, 1964; Spector, 1956). Several conditions have been shown to influence serum copper levels; serum copper is elevated during pregnancy (Chez et al., 1978), in women taking oral contraceptives (Shifrine and Fisher, 1976), and with the administration of hormones (Adelstein and Vallee, 1961; Johnson et al., 1969; Meyer et al., 1959). Serum copper is also elevated in several types of cancer including bronchogenic carcinoma; squamous cell carcinoma of the larynx; and cervical, breast and bladder cancer (Schwartz, 1975).

The highest tissue levels of copper are found in liver, heart, kidney and pancreas (2-5 mg/100 g dry tissue) (Vuori et al., 1978). Although females have lower concentrations of copper in tissue than males, the differences are not significant. The pancreas and skeletal muscles show a continuous decline in copper concentration with increasing age while the liver and kidney show decreasing concentrations up to maturity, then level off (Vuori et al., 1978).

Additional information on the metabolism, storage and excretion of copper by man and experimental animals can be found in Scheinberg and Sternlieb (1960), Adelstein and Vallee (1961), and NRC (1977).

3. Animal Studies

a. Carcinogenicity

An increase in occupational lung cancer among copper miners and smelters has been noted (Kuratsune et al., 1974; Tokudome and Kuratsune, 1976; Newman et al., 1976) but appears to be related to prolonged exposure to arsenic rather than to copper itself. Mortality from lung cancer among copper smelters was positively related to workers exposed to ore containing high levels of arsenic or to workers who had been involved in smeltering processes used prior to World War II (Tokudome and Kuratsune, 1976).

Reports on the effects of dietary copper on carcinogenesis and tumor growth have been varied. Elevated serum copper levels have been reported in humans with osteosarcoma (Fisher et al., 1976); Hodgkin's disease (Mitta and Tan, 1979); bronchogenic carcinoma; squamous-cell carcinoma of the larynx, and cancer of the bladder and cervix, and breast (Schwartz, 1975).

Fisher and co-workers (1976) noted elevated levels of serum copper in individuals with primary or metastatic osteosarcoma. The most elevated serum copper levels and the highest ratio of serum copper to serum zinc were found in patients with the more advanced disease (metastatic) and the poorest prognosis. However, in patients who were clinically tumor-free following amputation of osteosarcomatous limbs, serum copper levels were normal. In a later study (Shifrine and Fisher, 1976), these authors attempted to determine whether a similar elevation occurred in ceruloplasmin. They noted that the ratio of serum copper to ceruloplasmin was constant but that the concentration of ceruloplasmin was significantly increased in sera of patients with osteosarcoma compared with the sera of normal healthy individuals (80 mm^2vs. 52 mm^2 for controls). Presumably, the increased level of ceruloplasmin in patients with osteosarcoma is the reason for the elevated serum copper value noted in the earlier study.

Mitta and Tan (1979) also found elevated serum levels of copper in children with Hodgkin's disease; the highest levels were found in children diagnosed at the more advanced stages of the disease. Following treatment, however, serum copper was not a reliable measure of recurrence.

Similarly, Seto et al. (1978) found serum copper was augmented two to six times among rabbits with squamous-cell carcinoma as compared with animals with benign skin papillomas.

On the other hand, Santoliquido et al. (1976) found no significant difference ($p > 0.9$) in the copper concentration of 20 samples of malignant and noncancerous breast tissue (range 0.4-2.21, mean 0.96 vs. range 0.05-5.1, mean 0.94 μg/g wet tissue for noncancerous tissues).

Luthra et al. (1975, 1978) have monitored 2603 registered users of copper intrauterine devices (IUD) for periods up to 36 months for dysplastic lesions of the cervix or precancerous lesions. Only those women who had been followed up ± 2 mo. of scheduled follow-up were included for analysis. To date, a total of 158 women have been followed for 36 months of continuous copper-IUD use, 397 women for a period of 24 months. In a total of 2603 women examined, 95 dysplasia cases have been noted (56 initial and 39 developed during use). Out of these 95 cases, 59 could be followed up. More than 83% of these cases regressed to normalcy while 10 cases (17%) persisted as dysplasia. To date, no dysplastic case has progressed to cancer during the short study period. Further follow-up is currently underway.

The suppressive effect of copper on chemically-induced carcinogenesis in animals has been widely reported. Yamane and Sakai (1973) reported that concurrent administration of 0.5% copper acetate with the carcinogen 3'-methyl-4-(dimethylamino) azobenzene (3'-Me-DAB) in the diet of female Wistar rats for 7 months inhibited 3'-Me-DAB-induced heptocarcinogenesis. The incidences of liver tumors were 39, 0, and 0% for 3'-Me-DAB, copper alone or the combination, respectively.

Kamamoto _et al_. (1973) also found that the addition of 0.25% cupric acetate to the diet of male Wistar rats for a minimum of 12 weeks, inhibited the induction of ethionine-induced hepatomas. Yamane _et al_. (1976, 1977) found that the inhibitory activity was due to the direct interaction of copper with the rate of _in vivo_ ethylation of rat liver t-RNA and DNA by ethionine.

Petering and co-workers (1967) observed that both the anti-tumor activity and the toxicity of 3-ethoxy-2-oxobutyraldehyde bis (thiosemicarbazone) in rats bearing Walker 256 nitrogen-mustard-resistant carcinosarcoma was directly dependent on the dietary intake of cupric ion. Copper in the absence of drug was without effect.

In diets containing either 1 mg/kg copper (deficient) or 800 mg/kg copper (excessive), little difference was found in the induction of liver tumors in rats fed the carcinogen acetylaminofluorene (AAF) in the diet for 6 months, although the incidence of tumors at other sites was diminished. Similarly, the incidence of dimethylnitrosamine-induced hepatic neoplasms in rats on either copper deficient or excessive diets was unaffected. Kidney neoplasms, however, were absent on an excess copper-containing diet compared with an incidence of 57% in copper-deficient, dimethylnitrosamine-treated animals. No kidney neoplasms were present in control animals (Carlton and Price, 1973).

Burki and Okita (1969) also reported the addition of copper sulfate (198 mg/L) to the drinking water of mice had no effect on the incidence of 7,12-dimethylbenz (α)-anthracene-induced lymphomas or tumors of the lung and breast.

Thus, no experimental evidence exists to suggest that ingestion or localized absorption of copper is tumorigenic in either man or experimental animals. Indeed, several studies indicate that the administration of copper may inhibit tumor development. The significance of elevated serum copper levels in various types of cancer is unclear and remains to be elucidated.

b. Mutagenesis

Some indications of mutagenic effects of copper have been reported (Demerec _et al_., 1951; Law, 1938; Magrzhikovskaja, 1936; Loeb _et al_., 1977; Casto *et al.*, 1979). Demerec and co-workers (1951) noted an increase in back-mutations from streptomycin dependence to nondependence in *Escherichia coli* exposed to solutions of copper sulfate for three hours but only at concentrations which produced less than 5% survivors. For example, at a concentration of 0.00075% $CuSO_4$, 2.4% of the cells survived; mutation frequency was 40.5 mutants per 10^8 bacteria compared to 5.1 mutants per 10^8 bacteria in controls.

Law (1938) and Magrzhikovskaja (1936) have both demonstrated the capability of copper sulfate to increase the rate of lethal mutations in *Drosophila melanogaster*. Injection of a 0.1% solution of $CuSO_4$ and treatment of fertilized eggs with a concentrated aqueous solution of 10 minutes resulted in a mutation rate of 1 in 86.4 compared with 0 in 507 for controls (Law, 1938).

Loeb and co-workers (1977) found that copper ion at two or more concentrations increased the infidelity of DNA synthesis *in vitro* by more than 30 percent and scored copper as a positive mutagen. Infidelity during DNA synthesis may result in mutations.

Casto *et al*. (1979) recently noted that copper (.05-0.6 mM) also enhanced the transformation frequency of Syrian hamster embryo cells by a simian adenovirus, SA7. Hamster cells were either treated for 18 hrs prior to virus inoculation or 5 hrs after inoculation for a period of 48 hrs. Enhancement ratios of 2.2 and 16.2 were recorded for 0.08 mM $CuSO_4$ and 0.38 mM Cu_2S, respectively.

Negative findings were reported by Nishioka (1975) for a 0.05 M solution of $CuCl_2$ tested in a rec assay with *Bacillus subtilis*, strains H17 (Rec^+) and M45 (Rec^-).

In summation, information on the mutagenicity of copper is equivocal. Enhanced transformation of hamster embryo cells by a simian adenovirus is seen in the presence of copper and increased lethal mutations noted in *Drosophila*, but only at high concentrations. Bacterial assays are either negative or show mutagenic activity only at concentrations toxic to the bacterium. Further work is needed to clarify the mutagenic nature of copper, particularly in mammalian cells.

c. Adverse Reproductive Effects

Copper, when implanted into the uterus, is known to exert a contraceptive effect in both humans and experimental animals (Oster and Salgo, 1975; Hasson, 1978). Although the exact mechanism through which copper exerts its contraceptive action is unknown, the action is localized and implantation of the blastocyst does not occur (Ferm, 1976).

Chang and Tatum (1970) demonstrated that blastocysts briefly exposed to copper wire *in vitro* were able to develop when placed in normal uteri. However, blastocysts in copper-containing uteri disappeared before implantation occurred.

Subsequently, Brinster and Cross (1972) found that copper was toxic to the embryo. Exposure of two-celled mouse embryos in culture for 72 hrs to concentrations of 2.5×10^{-5} M $CuCl_2$ and higher was lethal, whereas embryos exposed to lower concentrations developed into blastocysts. In addition to killing the embryos, the higher concentrations of copper appeared to dissolve the zona pellucida of a few embryos.

Cuadros and Hirsch (1972) observed that the presence of metallic copper in the uterine cavity of rats or monkeys stimulated the local exudation of polymorphonuclear leukocytes. This mobilization may interfere with the maturation or survival of newly fertilized eggs.

Microscopic examination of uterine tissue from rats, rabbits and monkeys surgically implanted with copper intrauterine devices for 52 weeks revealed no lesions attributable to copper (Youkilis *et al*., 1973).

With respect to teratogenic effects, there is no evidence to suggest that intrauterine copper has a teratogenic effect on the exposed fetus (Hasson, 1978). Copper rings placed in the uteri of rats, hamsters and rabbits after implanation and left *in situ* throughout gestation did not produce teratogenic effects in the fetuses of those test animals (Chang and Tatum, 1973). In rats, however, insertion of a 5-7-mm copper ring into one horn of the uterus on day 6 of gestation increased the percentage of resorbed embyos (59.6%) compared with platinum-wire-implanted controls (25%) or untreated controls (13.9%). The average number of implantation sites and number of live fetuses were also decreased (i.e., 5.3, 6.0 and 6.5 implantation sites, and 2.8, 5.5 and 5.2 live births, respectively). The percentage of absorbed fetuses was found to increase in direct proportion to the length of time the copper wire was left *in situ* (Chang and Tatum, 1975).

In one animal study, intravenous injection of copper salts in pregnant golden hamsters (*Cricetus auratus*) on day 8 of gestation resulted in an increase in embryonic resorptions, as well as the appearance of developmental malformations in surviving offsprings (see Table 21). Copper in chelated form (copper citrate) was considerably more embryopathic than uncomplexed copper (copper sulfate) although embryocidal activities were similar. Malformations of the heart, especially ectopia cordis, appear to be a specific teratogenic effect of copper, particularly of the citrate complex. This may be the result of greater binding of uncomplexed copper to sites in the maternal system and thus its relative unavailability to the developing fetus (Ferm, 1976; Ferm and Hanlon, 1974).

Thus, copper exerts a localized contraceptive effect when implanted in the uterus. The exact mechanism of action is unclear but implantation of the blastocyst does not occur. Although toxic to the embryo, there is no evidence to suggest intrauterine copper is teratogenic. A single study did report developmental malformations in hamsters injected intravenously with high levels of copper on the eighth day of gestation.

TABLE 21. EFFECT OF COPPER SALTS ON EMBRYONIC DEVELOPMENT IN THE HAMSTER

Dose Level (mgCu/kg)	No. Mothers Treated	No. Gestation Sacs	No. Living Embryos (%)	No. Resorp-tions	No. Abnormal Embryos (%)
as Copper Sulfate					
2.13	16	210	155 (74)	55 (26)	12 (6)
4.25	3	49	7 (14)	42 (86)	4 (8)
7.5	3	30	0 (0)	22 (74)	-
10.0	2	maternicidal	-	-	-
as Copper Citrate					
0.25-1.5	13	172	143 (83)	29 (16)	4 (2)
1.8	6	81	48 (59)	33 (41)	14 (17)
2.2	8	99	65 (66)	34 (34)	35 (35)
4.0	2	maternicidal	-	-	-
Controls (demineralized water)					
0.5-1.0 ml/100g	10	125	115 (92)	10 (8)	0 (0)

SOURCE: Ferm and Hanlon, 1974.

d. Other Toxicological Effects

There is a wide margin of safety between copper deficiency and copper toxicosis in mammalian species, with the relative toxicity based on the efficiency of absorptive and excretory mechanisms (Venugopal and Luckey, 1978). Among mammals, copper toxicosis is more prominent in ruminants than nonruminants due to the interactions of copper, molybdenum and sulfate in ruminants; in nonruminants, the interactions of iron and zinc with copper predominate (NRC, 1977).

The acute oral toxicity of copper salts in laboratory animals ranges between 140 mg and 300 mg/kg depending on the salt; an oral mean lethal dose (LD_{50}) of 31 mg/kg, however, has been reported in guinea pigs (RTECS, 1977). Acute copper poisoning in mammals produces tachycardia, hypotension, hemolytic anemia, oliguria, uremia, coma, cardiovascular collapse and death (Venugopal and Luckey, 1978). Acute inhalation of copper produces congestion of nasal mucous membranes and ulceration and perforation of the nasal septum (Venugopal and Luckey, 1978). A list of acute LD_{50} values for various copper compounds is presented in Table 22.

Over prolonged periods of time, laboratory animals can tolerate up to 100 times the normal dietary intake of copper. Excessive intake of copper (about 300 to 500 times normal intake) by mammals leads to accumulation of copper in tissues, saturation of hepatic copper binding sites, and necrotic hepatitis. The extent of accumulation and subsequent toxicity depends upon the species; the dietary levels of zinc, iron, molybdate and sulfate; and the efficiency of the animals' excretory mechanisms (Venugopal and Luckey, 1978).

In rats, levels in excess of 250 mg copper/kg diet are required to produce toxicosis, and normal hepatic copper levels are maintained until a diet extremely high in copper (1000 mg/kg diet) is reached (NRC, 1977). Hepatic and renal necrosis have been observed in both rats and mice exposed to excessive copper levels (Lal and Sourkes, 1971; Vogel, 1960). Boyden et al. (1938) noted that rats fed 500 mg copper/kg diet as copper sulfate for 4 weeks were normal and exhibited good growth. At 1000 and 2000 mg/kg diet, growth and food intake were markedly depressed and spleen and liver copper levels at 4 weeks were markedly increased. Rats fed 4000 mg copper/kg diet died within 1 week.

e. Copper-Metal Interactions

The toxic effects of metals are often complicated by mutual biological antagonism of one metal with another at some functional site. For example, dietary zinc, copper and iron are so related that the balance of these nutrients is important in determining the metabolic effects of each other (Task Group on Metal Interactions, 1978).

The known antagonistic effects of cadmium on copper metabolism are probably due, at least in part, to inhibition of copper absorption (Campbell and Mills, 1974; Task Group on Metal Interactions, 1978).

TABLE 22. ACUTE TOXICITY OF COPPER COMPOUNDS

Compound	Species	Route	LD$_{50}$ (mg/kg)
Copper metal	Mouse	intraperitoneal	3.5
Copper(I) chloride	Human	oral	50 LDLo[1]
	Rat	oral	265
Copper(II) chloride	Rat	oral	140
	Mouse	oral	190
	Guinea pig	oral	31
	Mouse	intraperitoneal	7.4
Copper citrate	Rat	oral	1580
Copper hydroxide	Human	oral	200 LDLo[2]
Copper oxide	Rat	oral	470
Copper sulfate	Human (child)	oral	200 TDLo
	Human	oral	50 LDLo
	Rat	oral	300
	Mouse	intraperitoneal	7

---

[1] Lowest published lethal dose.

[2] Lowest published toxic dose (systemic effects).

SOURCE: RTECS, 1977

High levels of zinc interfere with copper absorption in rats (Van Campen and Scaife, 1967) while increases in the zinc to copper ratio increase plasma cholesterol levels in rats (Klevay, 1973).

Increases in dietary copper from 1 mg to 20 mg/kg diet were found to enhance the severity of lead toxicity in young male rats (Cerklewski and Forbes, 1977).

A complete discussion of these complex interactions is beyond the scope of this report but has been reviewed in detail by the Task Group on Metal Interactions, 1978; Magos, 1976; Sandstead, 1976; and Parizek, 1976. There are no available data on the relationship between intakes of copper, zinc and iron and the effects of cadmium in human populations (Task Group on Metal Interaction, 1978) but there is no question that the effects of copper are modified to some extent in the presence of other metals.

4. Human Studies

Copper toxicosis is rare in man. This is attributable to three factors: copper is an essential element in human nutrition, it is incompletely absorbed from the gastrointestinal tract; and milligram quanitities of ionic copper trigger an emetic action in man, thus preventing serious systemic toxicity. Exposure to copper generally occurs either by ingestion, inhalation, direct skin contact or from copper intrauterine devices.

a. Ingestion

Fatal copper poisoning is rare in man due to the emetic properties of copper, as well as the metallic taste. Acute copper poisonings have occurred, however, following ingestion of acidic food or drink that was in prolonged contact with the metal or ingestion of a large quantity (several grams) of a copper salt where vomiting failed to occur (NRC, 1977). For example, a 44-year-old woman with a partial gastrectomy failed to vomit 10 ml of a 10% solution of copper sulfate (~ 400 mg Cu^{++}) given to her as an emetic. Despite gastric lavage, the woman died 6 days later with respiratory, renal and hepatic failure, hemolytic anemia and gastrointestinal hemorrhage (Stein et al., 1976). On the other hand, Walsh and co-workers (1977) reported the survival with treatment of an 18-month-old boy who ingested approximately 3 g of copper sulfate (~ 1200 mg Cu^{++}). Renal tubular damage and hemolytic anemia appeared during the acute phase of poisoning, but the child appeared "clinically" well within 5 days.

Chugh et al. (1977) also reported acute renal failure in 11 of 29 suicidal patients with acute copper sulfate poisoning (ingested between 1 g and 50 g). Intravascular hemolysis appeared to be the chief factor responsible for renal lesions in these patients and, despite dialysis, only 6 of 11 patients recovered.

It is believed that the mishandling of copper following its accumulation by high copper intake would produce similar symptoms as are observed in patients with Wilson's disease, a hepatolenticular degenerative disorder of copper metabolism. This disease, inherited as an autosomal recessive trait, is characterized by a two-phase process involving passive accumulations of copper in the liver over an extended period followed by the sudden release of this stored copper, generally described as the hemolytic crisis. Symptoms include tremor, ascites, psychosis, slurring of speech, and eventual hepatic necrosis and schlerosis of the corpus striatum, brain trauma and death (Bremner, 1974; Venugopal and Luckey, 1978).

b. Inhalation

"Vineyard sprayer's disease" is known to occur in workers exposed to fungicidal sprays containing copper sulfate. Pulmonary copper deposition, as an apparently local effect, occurs in the lungs of vineyard workers after years of exposure. Blue areas of the lung, noted at autopsy, suggest the presence of excess copper. Hepatic lesions are also present, including focal or diffuse swelling and proliferation of Kupffer cells, histocytic or sarcoid-like granulomas, liver fibrosis and cirrhosis (Pimental and Menezes, 1977).

c. Dermal Exposure

A case of acute copper poisoning resulting from the absorption of copper sulfate from burned dermal tissue was reported by Holtzman et al., 1966. A $5^1/_2$-year old girl burned over 30-40% of her body developed icterus, oliguria and hemolytic anemia within 24 hrs of the seventh debridement with copper sulfate crystal over a 9-week period. Her serum ceruloplasmin and copper rose to 86 mg/100 ml and 540 μg/100 ml, respectively. Treatment with fresh whole blood and chelating agents cleared the symptoms within 24 hrs, but serum levels of copper and ceruloplasmin remained moderately elevated for 6 months after treatment.

Although relatively uncommon, dermal contact with copper can provoke allergic skin reactions in some individuals. Contact dermatitis has been reported following contact with copper-containing jewelry (Saltzer and Wilson, 1968), dental cement (Martindale, 1977), and copper wire (Forstrom et al., 1977).

Eczematous-type dermatitis has also been reported from uterine contact with copper intrauterine devices (Barkoff, 1976; Dry et al., 1978). Barkoff (1976) reported that a 24-year-old woman developed severe acute urticaria, joint pain and marked angioedema secondary to a copper intrauterine contraceptive device inserted 1 month previously. Allergy to copper was proven by scratch tests with 1% copper sulfate solution. The condition cleared subsequent to removal of the device.

d. Copper Intrauterine Devices (IUD's)

In that the experience with copper-containing IUD's is of relatively limited duration (10 years), definitive assertions cannot be made concerning long-term effects. However, at present there is no evidence to indicate that copper IUD's adversely affect future fertility, or that they increase carcinogenic or teratogenic risks in humans. The local, systemic and contraceptive effects of copper IUD's have been widely studied and are extensively reviewed by Hasson (1978), and Oster and Salgo (1975, 1977).

Hagenfeldt (1972) reported that the average loss of copper from a copper IUD (200 mm^2) was 50 μg/day and further, that only the endometrial copper levels were elevated and that these returned to normal within the first cycle following removal of the device. Other investigators have noted no elevation of serum copper levels in users of copper IUD's (Anteby *et al.*, 1978; Elstein and Daunter, 1973).

Menstrual blood collected from women using copper IUD's contains about one-half of the total copper lost from the device during 1 month (Oster and Salgo, 1975). Thus, approximately 750 μg of copper per month are retained and presumably absorbed into the circulation. Although this is only a small fraction of ingested dietary copper, possibly retention over the years or decades a woman is likely to use intrauterine devices could produce some adverse effects in susceptible individuals.

To date, only a few births have occurred in women who retained a copper IUD throughout pregnancy; the infants appear normal (Tatum, *et al.*, 1976; Hasson, 1978). However, involuntary pregnancies with a copper IUD *in utero* have a greater chance of ending in spontaneous abortion. Tatum *et al.* (1976) noted the incidence of spontaneous abortion more than doubled (54%) in 157 women who elected to retain IUD *in situ* when compared with 118 women who either expelled or had the device removed (23%). Tatum's data also suggested an increased risk of having an ectopic pregnancy in women who had worn a copper-T device for more than 2 years. Only one anomaly (benign fibroma of the vocal cords) was found in 166 infants born of women who conceived while using a copper-IUD and who continued the pregnancy with the device *in situ* (Tatum *et al.*, 1976).

A summary of the outcome of pregnancies with copper IUD's followed to termination is presented in Table 23.

5. Overview

Copper is an essential nutrient for man and animals and plays a vital role in numerous biochemical and physiological functions. Since most human diets contain an over-abundant supply of copper, human copper deficiency is extremely rare.

TABLE 23. OUTCOME OF PREGNANCIES WITH COPPER IUD's FOLLOWED TO TERMINATION

No.	Induced Abortions	Non-Induced Abortions (%)			Live-Births	Source
		Spontaneous	Ectopic	Stillbirth		
57	32 (56%)	44	0	0	56	Snowden, 1975
374	198 (53%)	30	5	-	65	Stewart *et al*. 1975
773	465 (60%)	37	9	1	53	Tatum *et al*. 1976

SOURCE: Adapted from Hasson (1978)

In man, approximately 30% of ingested copper is absorbed, but because copper is excreted into bile, which is not reabsorbed, effective net absorption is about 5%. Roughly 95% of ingested copper is eliminated in the feces (70% ingested but unabsorbed; 25% biliary excretions of absorbed copper), with small amounts excreted in urine and sweat.

There is no experimental evidence to suggest that copper is a carcinogen and it may in fact, inhibit some types of chemically induced tumors in laboratory animals. Some indications of mutagenicity have been reported for copper but generally at toxic concentrations. Further work is needed to clarify this issue.

Copper, when implanted into the uterus, exerts a contraceptive effect in both humans and experimental animals. The release of copper is localized, although some degree of systemic absorption of copper occurs. There is no evidence to suggest that intrauterine copper is either teratogenic or impairs future fertility in humans. A single study noted increased embryonic resortions and developmental malformations in surviving offspring of hamsters injected intravenously with copper salts on day 8 of gestation.

Toxicological studies with nonruminant animals indicate little toxicity except at dietary levels far in excess of normal intake. Depending on the salt, acute oral LD_{50} values for most species range from 140 mg/kg to 300 mg/kg. Copper toxicosis in humans in also unusual and is generally linked to suicidal ingestion of large quantities of copper or to individuals with genetic defects in copper metabolism.

B. HUMAN EXPOSURE

1. Introduction

The previous section on the effect of copper on humans indicates that it has a very low order of toxicity. In fact, most discussions regarding human exposure to copper emphasize deficiency, as opposed to effects resulting from large doses. As a result, this section will not go into great detail in estimating copper exposure to various subpopulations. It will attempt to provide order to magnitude estimates for exposure to copper through various routes.

2. Ingestion

a. Food

NRC (1977) has reviewed the copper content of various foods extensively, as this subject has been looked into in some detail. Foods particularly high in copper include oysters, organ meats, and dried legumes. Holden et al. (1979) recently surveyed the copper intakes of 12 subjects. They analyzed composites of self-selected diets, including beverages and drinking water over a 14-day period. The overall mean daily intake was 1.0 ± 0.1 mg, well below the suggested U.S. Recommended Daily Allowance (RDA) of 2 mg. The highest daily intake reported was 2.41 mg, although none of the diets contained oysters or organ meats. These results are shown in Table 24, along with other data reported on copper intakes. It is apparent from these data that consumption is generally less than 2 mg/day, although persons consuming diets with liver consumed 7.6 mg copper/day.

The addition of 15 mg/kg copper to livestock feed is allowed by FDA and is a common practice. However, the feedstock may already contain adequate levels of copper. This practice may result in the accumulation of copper in animal livers, especially sheep, swine and poultry (NRC, 1977). These authors also point out that baby food made from liver containing 550 ppm copper (wet weight) would result in an exposure of 15 mg per 1-oz serving. The prevalence of this exposure is unknown.

b. Drinking Water

Levels of copper in drinking water depend on levels in water supply, treatment efficiency, and the use of copper in the distribution system. Concentrations vary geographically, as well as by water type (hard vs. soft), water temperature, and length of time standing in pipes. In general, higher concentrations are found in areas with soft water (Schroeder et al., 1966). The U.S. DHEW (1970) reported that the maximum concentration reported in 2595 distribution samples was 8.35 mg/L copper. However, only 1.6% of the samples exceeded the recommended drinking water standard of 1 mg/L and the mean concentration was 0.134 mg/L.

The study conducted by Holden et al. (1979) included drinking water in the calculated intake, although drinking water concentrations may have been low in the area of the test. It is unknown whether the other surveys shown in Table 24 included drinking water; however, they probably did not Therefore, a maximum exposure of 24 mg copper/day could occur, resulting from consumption of a diet high in copper-rich foods and from drinking water very high in copper. Such an exposure would appear to be limited to a very small subpopulation. A more general ingestion exposure would be in the range of 1-4 mg/day.

3. Inhalation

EPA (1979) has reviewed the potential for copper exposure through inhalation. A survey of ambient air concentration in rural and urban communities showed concentrations of 0.01 $\mu g/m^3$ and 0.257 $\mu g/m^3$, respectively (National Air Pollution Control Administration 1968 as cited in EPA, 1979). Concentrations in areas where high concentrations would be expected such as near smelters, are 1-2 $\mu g/m^3$ (EPA, 1979). Thus, a maximum inhalation exposure would be .04 mg/day, considerably lower than ingestion exposure.

TABLE 24. DIETARY INTAKES OF COPPER REPORTED IN THE LITERATURE

Intake (mg/day)	Type of Diet	Number of Subjects	Reference
0.34	self-selected (24-hr)	4 female	White (1969)
0.91	self-selected	1 female	Tipton *et al*. (1966)
1.0	self-selected	11 male, 11 female	Holden *et al*. (1979)
1.04	self-selected	36 female	Tipton *et al*. (1966)
1.2	Non-institutional diets	12 female	Guthrie and Robinson (1977)
1.5	diets (no liver)	12 female	Guthrie and Robinson (1977)
1.8-2.1	balance study	11 female	Robinson *et al*. (1973)
1.9	institutional diet	12 female	Guthrie and Robinson (1977)
2.4	self-selected	12 female	Guthrie (1973)
3.8	diet composites	1 male	Zook and Lehman (1965)
7.6	diets (with liver)	11 female	Guthrie and Robinson (1977)

SOURCE: Holden *et al*. (1979)

4. Medical Exposure

Exposures to copper have been reported for persons applying copper sulfate to large areas of burned skin. Such incidents were described in the preceding section and appear to be rare.

Persons receiving dialysis have also been exposed to copper, primarily due to high levels in source water or equipment problems. While these incidents appear to be rare, an exposure of 5 mg over a 7-hr dialysis-day has been reported (Blomfield *et al.*, 1969). Using a maximum tap-water level of 1 mg/L, these authors calculated potential exposure of 240 mg, using a 240-L volume for dialysis. However, this exposure assumes a total uptake of copper by the blood, which is probably unlikely. Most of the equipment problems with dialysis were reported 10 or so years ago, and a literature search did not uncover any more recent problems. Therefore, it is not clear whether these problems have been assumed to be insignificant or more likely, equipment has been improved to reduce exposure.

A more common exposure route is through the use of copper IUD's. It has been shown that a 200-mm^2 copper device releases 50 µg copper/day as cupric ions in free or complexed form (Hagenfeldt, 1972). As discussed in the previous section, about one-half of the released copper is lost in menstrual blood. The resultant exposure of approximately .025 mg/day cannot be directly compared with ingestion exposure since presumably this release is available for absorption. while only about 5% of ingested copper is absorbed. However, increased serum copper levels due to the use of copper IUD's have not been reported.

5. Conclusions

Food is the primary source of copper for most people; however, contributions from drinking water may be important in a few locations. In general, exposure would be in the range of 1-4 mg/day. Persons eating diets comprised of copper-rich foods and/or living in areas with high drinking water levels would receive higher copper exposures up to 24 mg/day. In addition, dialysis patients, as well as copper IUD users, may receive slightly higher exposure to copper.

REFERENCES

Adelstein, S.J. and B.L. Vallee. 1961. Copper metabolism in man. New Engl. J. Med. 265:892-97.

al-Rashid, R.A. and J. Spangler. 1971. Neonatal copper deficiency. N. Engl. J. Med. 285:841-43.

Anteby, S.O., H.A. Ben Bassat, S. Yarkoni, Y. Aboulafia and E. Sadousky. 1978. The effect of intrauterine devices containing zinc and copper on their levels in serum. Fertil. Steril. 29(1):30-34.

Barkoff, J.R. 1976. Urticaria secondary to a copper intrauterine device. Int. J. Dermatol. 15(8):594-95.

Bloomfield, J., J. McPherson, and C.R.P. George. 1969. Active uptake of copper and zinc during haemodialysis. B. Med. J. 1(650):141-145.

Boyden, R., V.R. Potter and C.A. Elvehjem. 1938. Effect of feeding high levels of copper to albino rats. J. Nutr. 15:397-402.

Bremner, I. 1974. Heavy metal toxicities. Quart. Rev. Biophys. 7(1):75-124.

Brinster, R.L. and P.C. Cross. 1972. Effect of copper on the preimplantation mouse embryo. Nature 238:389-99.

Burki, H.R. and G.T. Okita. 1969. Effect of oral copper sulfate on 7,12-dimethylbenz anthracene carcinogenesis in mice. Br. J. Cancer 23(3):591-96.

Campbell, J.K. and C.F. Mills. 1974. Effects of dietary cadmium and zinc on rats maintained on diets low in copper. Proc. Nutr. Soc. 33(1):15A-16A.

Carlton, W.W. and P.S. Price. 1973. Dietary copper and the induction of neoplasms in the rat by acetylaminofluorene and dimethylnitrosamine. Food Cosmet. Toxicol. 11(5):827-40.

Cartwright, G.E. and M.M. Wintrobe. 1964. Copper metabolism in normal subjects. Am. J. Clinical Nutr. 14:224-32 as cited in Vuori et al., 1978.

Casto, B.C., J. Meyers and J.A. DiPaolo. 1979. Enhancement of viral transformation for evaluation of the carcinogenic or mutagenic potential of inorganic metal salts. Cancer Research 39: 193-198.

Caudros, A. and J.G. Hirsch. 1972. Copper on intrauterine devices stimulates leukocyte exudation. Science 175:175-76.

Cerklewski, F.L. and R.M. Forbes. 1977. Influence of dietary copper on lead toxicity in the young male rat. J. Nutr. 107(1):143-46.

Chang, C.C. and H.J. Tatum. 1970. A study of the antifertility effect of intrauterine copper. Contraception 1:265 as cited in Hasson, 1978.

Chang, C.C. and H.J. Tatum. 1973. Absence of teratogenicity of intrauterine copper wire in rats, hamsters and rabbits. Contraception 7:413 as cited in Hasson, 1978.

Chang , C.C. and H.J. Tatum. 1975. Effect of intrauterine copper wire on resorption of fetuses in rats. Contraception 11(1):79-84.

Chez, R.A., R.I. Henkin, and R. Fox. 1978. Amniotic fluid copper and zinc concentrations in human pregnancy. Obstet. Gynecol. 52(1):125-27.

Chugh, K.S., B.K. Sharma, P.C. Singhal, K.C. Das, B.N. Datta. 1977. Acute renal failure following copper sulfate intoxication. Postgrad. Med. J. 53(615):18-23.

Demerec, M., G. Bertani, J. Flint. 1951. A survey of chemicals for mutagenic action on E. coli. Am. Nat. 85:119-36.

Dry, J., F. Leynadier, A. Bennani, P. Piquet and J. Salat. 1978. Intrauterine copper contraceptive devices and allergy to copper and nickel (letter). Ann. Allergy 41(3):194.

Dunlap, W.M., G.W. James III and D.M. Hume. 1974. Anemia and neutropenia caused by copper deficiency. Ann. Intern. Med. 80:470-76 as cited in Graham and Cordano, 1976.

Elstein, M. and B. Daunter. 1973. Copper absorption from I.U.C.D.s Brit. Med. J. 2:776.

Ferm, V.H. 1976. Teratogenic effects and placental permeability of heavy metals. Curr. Top. Pathol. 62:145-51.

Ferm, V.H. and D.P. Hanlon. 1974. Toxicity of copper salts in hamster embryonic development. Biol. Reprod. 11(1):97-101.

Fisher, G.L., V.S. Byers, M. Shifrine and A.S. Levin. 1976. Copper and zinc levels in serum from human patients with sarcomas. Cancer 37(1):356-63.

Forstrom, L., R. Kiistala, K. Tarvainen. 1977. Hypersensitivity to copper verified by test with 0.1% $CuSO_4$. Contact Dermatitis 3(5):280-81.

Frommer, D.J. 1977. Biliary copper excretion in man and the rat. Digestion 15(5):390-96.

Goodman, L.S. and A. Gilman. 1975. The Pharmacological Basis of Therapeutics. Fourth Edition. The MacMillan Company, Collier-MacMillan Canada Limited, Toronto. pp. 1409-10.

Graham, G. and A. Cordano. 1976. Copper deficiency in human subjects. Chap. 22 in: Trace Elements in Human Health and Disease, Vol. 1, Zinc and Copper. A.S. Prasad, ed. Academic Press, New York, pp. 363-372.

Guthrie, B. and M.F. Robinson. 1977. Daily intake of manganese, copper, zinc, and cadmium by New Zealand women. Br. J. Nutr. 38:55 as cited in Holden et al. (1979).

Guthrie, B.E. 1973. Daily dietary intake of zinc, copper, manganese, chromium, and cadmium by some New Zealand women. Proc. Univ. Otago Med. School. 51:47 as cited in Holden et al. (1979).

Hagenfeldt, K. 1972. Intrauterine contraception with the copper-T device. I. Effect on trace elements in the endometrium, cervical mucus and plasma. Contraception 6:37-54.

Hasson, H.M. 1978. Copper IUDs. J. Reprod. Med. 20(3):139-54

Holden, J.M., W.R. Wolf, and W. Mertz. 1979. Zinc and copper in self-selected diets. J. Am. Diet. Assoc. 75:23-28.

Holtzman, N.A., D.A. Elliot, R.H. Heller. 1966. Copper intoxication Report of a case with observations on ceruloplasmin. N. Engl. J. Med. 275:347-52.

Iwanska, S. and D. Strusinska. 1978. Copper metabolism in different states of erythropoiesis activity. Acta. Physiol. Pol. 29(5):465-74.

Johnson, N.C., T. Kheim, and W.B. Kountze. 1959. Influence of sex hormones on total serum copper. Proc. Soc. Exper. Biol. and Med. 102:98 as cited in Adelstein and Vallee (1971).

Kamamoto, Y., S. Makiura, S. Sugihara, Y. Hiasa, M. Arai, and K. Ito. 1973. The inhibitory effect of copper on DL-ethionine carcinogenesis in rats. Cancer Res. 33:1129-35.

Karpel, J.T. and V.H. Peden. 1972. Copper deficiency in long-term parenteral nutrition. J. Pediat. 80:32-36 as cited in Graham and Cordano, 1976.

Klevay, L.M. 1973. Hypercholesterolemia in rats produced by an increase in the ratio of zinc to copper ingested. Am. J. Clin. Nutr. 26:1060-68.

Kuratsune, M., S. Tukodome, T. Shirakusa, M. Yoshida, Y. Tokumitsu, T. Hayano, and M. Seita. 1974. Occupational lung cancer among copper smelters. Int. J. Cancer 13(4):552-58.

Lal, S. and T.L. Sourkes. 1971. Deposition of copper in rat tissues - The effect of dose and duration of administration of copper sulfate. Toxicol. Appl. Pharmacol. 20:269-83.

Law, L.W. 1938. The effects of chemicals on the lethal mutation rate in Drosophila melanogaster. Proc. Nat. Acad. Sci. 24:546-50.

Lee, G.R., D.M. Williams, G.E. Cartwright. 1976. Role of copper in iron metabolism and heme synthesis. Chap. 23 in: Trace Elements in Human Health and Disease, Vol. 1, Zinc and Copper, A.S. Prasad, ed. Academic Press, New York, pp 373-90.

Linder, M.C. 1977. Iron and copper metabolism in cancer, as exemplified by changes in ferritin and ceruloplasmin in rats with transplantable tumors. Adv. Exp. Med. Biol. 92:643-64.

Loeb, L.A., M.A. Sirover, L.A. Weymouth, D.K. Dube, G. Seal, S.S. Agarwal and E.Katz. 1977. Infidelity of DNA synthesis as related to mutagenesis and carcinogenesis. J. Toxicol. Environ. Health 2:1297-1304.

Luthra, M.K., A.B. Mitra, G. Bhinder, P. Bhatnagar and N.C. Saxena. 1975. Surveillance for carcinogenesis in women using copper intra-uterine device for contraception. Indian J. Med. Res. 63(12):1787-93.

Luthra, U.K., A. B. Mitra, A.K. Prabhaker, P. Bhatnagar and S.S. Agarwal. 1978. Role of copper IUD in cervical carcinogenesis: A follow-up of 36 months. Indian J. Med. Res. 68:78-83.

Magos, L. 1976. "The role of synergism and antagonism in the toxicology of metals". Chapter C1, pp 491-97 in: Effects and Dose-Response Relationships of Toxic Metals. G.F. Nordberg, ed. Elsevier Scientific Publishing Co., Amsterdam.

Magrisukovskaya, K.V. 1936. Bull. Biol. Med. Exp., I. as cited in Law, 1938.

Martindale: The Extra Pharmacopoeia. 1977. Twenty-seventh edition. A. Wafe, ed., The Pharmaceutical Press, London, pp 893-95.

Meyer, B.J., A.C. Meyer and M.K. Horwitt. 1959. Effect of tri-iode thyronine on serum copper and basal metabolism in schizophrenic patients. Arch. Gen. Psychiat. 1:374-78 as cited in Adelstein and Vallee, 1961.

Mitta, S.K. and C. Tan. 1979. Serum copper levels (SCL) in children with Hodgkin's disease (HD). (Meeting abstract) Proc. Am. Assoc. Cancer Res. 20:382.

National Air Pollution Control Administration. 1968. Air quality data from the National Air Surveillance Networks and contribution of State and local networks. 1966 ed. NAPLA Publ., APTD-68-9. As cited in EPA (1979).

Newman, J.A., V.E. Archer, G. Saccomanno, M. Kuschner, O. Auerbach, R.D. Grondahl and J.C. Wilson. 1976. Histologic types of bronchogenic carcinoma among members of copper-mining and smelting communities. Ann. N.Y. Acad. Sci. 271:260-68.

Nishioka, H. 1975. Mutagenic activities of metal compounds in bacteria. Mutat. Res. 31:185-89.

NRC (National Research Council). 1977. Copper. PB 279307, 115 pp. National Academy of Sciences, Washington, D.C.

O'Dell, B.L., B.C. Hardwick, and G. Reynolds. 1961. Mineral deficiencies of milk and congenital malformations in the rat. J. Nutr. 73:151-57.

O'Dell, B. 1976. "Biochemistry and Physiology of copper in vertebrates". Chap. 24 in: Trace Elements in Human Health and Disease, Vol. 1, Zinc and Copper, A.S. Prasad, ed. Academic Press, New York, 1976.

Oster, G. and M. Salgo. 1975. The copper intrauterine device and its mode of action. N. Engl. J. Med. 293:432-38.

Oster, G. and M.P. Salgo. 1977. Copper in mammalian reproduction. Adv. Pharmacol. Chemother. 14:327-409.

Parizek, J. 1976. "Interrelationships among trace elements". Chapter C2, pp 498-510 in: Effects and Dose-Response Relationships of Toxic Metals. G.F. Nordberg, ed. , Elsevier Scientific Publishing Co., Amsterdam.

Petering, H.G., H. H. Buskirk and J.A. Crim. 1967. The effect of dietary mineral supplement on the rat on the antitumor activity of 3-ethoxy-2-oxybutyraldehyde bis(thiosemicarbazone). Cancer Res. 27:1115-21.

Pimental, J.C. and A.P. Menezes. 1977. Liver disease in vineyard sprayers. Gastroenterology 72(2):275-83.

Robinson, M.F., J.M. McKenzie, C.D. Thomson, A.L. vanRij. 1973. Metabolic balance of zinc, copper, cadmium, iron, molybdenum, and selenium in young New Zealand women. Br. J. Nutr. 30:195 as cited in Holden et al. (1979).

RTECS (Registry of Toxic Effects of Chemical Substances). 1977. Vol. II. E.J. Fairchild, R.J. Lewis, Sr., and R.L. Tatkon, eds. U.S. DHEW, NIOSH 78-104-B.

Saltzer, E.I. and J.W. Wilson. 1968. Archs. Derm. 98:375 as cited in: Martindale, 1977.

Sandstead, H.H. 1976. "Interactions of cadmium and lead with essential minerals". Chap. C3, pp 511-26 in: Effects and Dose-Response Relationships of Toxic Metals. G.F. Nordberg, ed., Elsevier Scientific Publishing Co., Amsterdam.

Santoliquido, P.M., H.W. Southwickand J.H. Olwin. 1976. Trace metal levels in cancer of the breast. Surg. Gynecol. Obstet. 142(1):65-70.

Scheinberg, H. and I. Sternlieb. 1960. Copper metabolism. Pharmacol. Rev. 12:355-31.

Schroeder, H.A., A.P. Nason, I.H. Tipton, and J.J. Balassa. 1966. Essential trace metals in man: copper. J. Chron. Dis. 19:1007-1034

Schwartz, M.K. 1975. Role of trace elements in cancer. Cancer Res. 34:3481-87.

Seto, A., H. Tokuda, Y. Ito. 1978. Malignant conversion of Shope papillomas and associated changes of serum ceruloplasmin in domestic rabbits. Proc. Soc. Exp. Biol. Med. 157(4):694-96.

Shifrine, M. and G.L. Fisher. 1976. Ceruloplasmin levels in sera from human patients with osteosarcoma. Cancer 38(1):44-48.

Snowden, R. 1975. Pelvic inflammation, perforation and pregnancy outcome associated with the use of IUDs. In: Analysis of Intrauterine Contraception, pp. 139-46. North Holland Publishing Co., as cited in Hasson, 1978.

Spector, W.S. 1956. Handbook of Biological Data: Prepared under the direction of the Committee on the Handbook of Biological Data - Division of Biology and Agriculture, the National Academy of Sciences, the National Research Council. Philadelphia, Saunders, 408 pp. as cited in Adelstein and Vallee, 1961.

Stein, R.S., D. Jenkins and M. Korrs. 1976. Death after use of cupric sulfate as emetic. JAMA 235:801 (letter.)

Stewart, W.C., F.B. O'Brien, C. Nisson et al. 1975. Multiclinic evaluation of Gravigard (Cu7) intrauterine contraception. In: Analysis of Intrauterine Contraception, pp 149-53, North Holland Publishing Co., as cited in Hasson, 1978.

Task Group on Metal Interaction, Scientific Committee on the Toxicology of Metals. 1978. Factors influencing metabolism and toxicity of metals: A consensus report. International Association on Occupational Health. Environ. Health Perspect. 25:3-41.

Tatum, H.J., F.H. Schmidt and A.K. Jain. 1976. Management and outcome of pregnancies associated with the copper-T intrauterine contraception device. Am. J. Obstet. Gynecol. 126:869-74.

Tipton, I.H., P.L. Stewart, and P.G. Martin. 1966. Trace elements in diets and excreta. Health Phys. 12:1683 as cited in Holden et al. (1979).

Tokudome, S. and M. Kuratsune. 1976. A cohort study on mortality from cancer and other causes among workers at a metal refinery. Int. J. Cancer 17(3):310-17.

Ulmer, D.C. 1977. Trace Elements. N. Engl. J. Med. 297(6)318-21.

U.S. Department of Health Education and Welfare (U.S. DHEW). 1970. Community Water Supply Study. Public Health Service, Environmental Health Service, Bureau of Water Hygiene.

U.S. EPA. 1979. Ambient water quality criteria: Copper. Criteria and Standards Div., Office of Water Planning and Standards.

Van Campen, D.R. and P.U. Scaife. 1967. Zinc interference with copper absorption in rats. J. Nutr. 91:473-76.

Venugopal, B. and T.D. Luckey. 1978. Metal Toxicity in Mammals. 2. Chemical toxicity of metals and metalloids. Plenum Press, New York, pp 24-32.

Vogel, F.S. 1960. Nephrotoxic properties of copper under experimental conditions in mice, with special reference to the pathogenesis of the renal alterations in Wilson's disease. Amer. J. Pathol. 36:699-711.

Vuori, E., A. Huernan-Seppala, and J.O. Kilpio. 1978. Biologically active metals in human tissues. I. The effect of age and sex on the concentration of copper in aorta, heart, kidney, liver, lung, pancreas and skeletal muscle. Scand. J. Work Environ. Health 4(2):167-75.

Walsh, F.M., F.J. Brosson, M. Bayley, J. McReynolds and B.J. Pearson. 1977. Acute copper intoxication. Pathophysiology and therapy with a case report. Am. J. Dis. Child. 131(2):149-51

White, H.S. 1969. Inorganic elements in weighed diets of girls and young women. J. Am. Dietet A. 44:38 as cited in Holden et al. (1979).

Yamane, Y. and K. Sakai. 1973. Suppressive effect of concurrent administration of metal salts on carcinogenesis by 3'-methyl-4-(dimethylamine)azobenzene, and the effects of these metals on aminoazo dye metabolism during carcinogenesis. Gann 64(6):563-73.

Yamane, Y., K. Sakai, and S. Kojima. 1976. Mechanism of the suppressive effect of basic cupric acetate on rat liver carcinogenesis caused by ethionine. Gann 67:295-302

Yamane, Y., K. Sakai, M. Shibata and K. Chiba. 1977. Suppressive effect of copper on ethylation of rat liver DNA with ethionine in vivo. Gann 68(5):713.

Youkilis, G.J., R.G. McConnell, R.D. Hemm and J.M. Andress. 1973. Toxicity studies of a copper-containing intrauterine device in several laboratory animal species. Toxicol. Appl. Pharmacol. 25(3):463-64.

Zook, E. and J. Lehman. 1965. Total diet study: Content of ten minerals--aluminum, calcium, phosphorus, sodium, potassium, boron, copper, iron, manganese, and magnesium. J. Assoc. Off. Agric. Chem. 48:850 as cited in Holden et al. (1979).

VII. RISK CONSIDERATIONS

A. BIOTA

The risk of copper exposure for aquatic biota varies widely from location to location. The potential for exposure to acutely toxic concentrations may occur when very high concentrations of copper are released into a water body, such as when chemical wastes are spilled or discharged. In such cases, the effects on aquatic life may be localized with the degree of impact dependent upon the nature of the receiving water body (dilution volume, availability of complexing agents, etc.). For large regions of the country, chronic exposure can be anticipated in areas in which certain conditions (or combinations of conditions) prevail, i.e., acidic or soft water, high copper levels, and sensitive species. Table 25 lists the major river basins in which the potential risk of adverse effects is greater because of high copper levels or soft water. It is likely, however, that risk is limited to a member of very localized areas within these larger basins.

Based on laboratory studies, species of aquatic biota appear to vary considerably in their sensitivity to harmful effects of copper. As a group, the salmonids are probably the species mot sensitive to aqueous copper, exhibiting toxicosis when exposed to copper concentrations of 10 μg/L in soft water. However, some warmwater fish such as the fathead minnow are also susceptible to relatively low concentrations of copper (23 μg/L in very soft water). Based on STORET monitoring data, they are exposed to total copper levels at least this high in many parts of the regions in which they are found. Aquatic vertebrates tend to be most sensitive to copper in the embryo and larval stages, and most resistant as eggs and adults. The daphnids appear to be particularly sensitive to copper. Certain species of Chlorella algae are the most sensitive of the plant species tested.

The data presented previously in Sections IV and V concerning the effects of and exposure to copper suggest that there is a widespread potential in the U.S. for exposure to harmful levels of copper. However, conclusions cannot be reached about the risks of copper exposure on the basis of monitoring data and laboratory toxicity studies alone. Although the environmental fate of copper has been discussed previously (in Section IV), it is important to review certain aspects of environmental pathways and chemical characteristics of copper in order to understand the implications of these factors for risk to biota.

Toxicity studies have made it apparent that some species of copper are responsible for the observed effects and others are not. Toxicity to some algae and invertebrates has been shown to be a function of cupric ion activity (Jackson and Morgan, 1978; Anderson and Morel, 1978; Andrew et al., 1977; and Van den Berg et al., 1979). Shaw and Brown (1974) related the toxicity of copper to Cu^{2+} and $CuCO_3^{\circ}$ for rainbow trout.

TABLE 25. RIVER BASINS WITH FACTORS CONTRIBUTING TO RISK FOR AQUATIC ORGANISMS

River Basins with Soft Water

New England

Northern California

Pacific Northwest

Southeast (except Florida)

River Basins with High Aqueous Copper Concentrations*

Lower Colorado	36%
New England	23%
Western Gulf	18%
Southeast	17%
Upper Mississippi	17%
Rio Grande and Pecos	14%

River Basins with High Copper Concentrations in Sediment**

Hawaii	67%
Souris and Red of North	35%
Lower Colorado	20%
Great Lakes	19%
Upper Mississippi	19%
New England	16%
Mid Atlantic	15%

* Percentage of samples exceeding 100 μg/L total copper
** Percentage of samples exceeding 100 mg/kg total copper
Source: STORET (1970-1979)

Brown et al. (1974) reported that the toxic effects of copper could be mitigated through the addition of various types of organic materials. Howarth and Sprague (1978), as well as Chakoumakos et al. (1979), concluded that the copper ion, as well as the hydroxy complexes, are toxic to cutthroat trout and rainbow trout. Thus, it is clear that some forms of copper are not toxic to aquatic organisms. However, it has not been determined which additional species are toxic besides the cupric ion. In addition, it has generally been assumed that suspended copper is not available or toxic, since it would be either strongly adsorbed or complexed. (Shaw and Brown, 1974; Brungs et al. 1976).

The monitoring data reported here are for total copper. The levels measured may bear little relation to the results of laboratory toxicity studies for a number of reasons. First, only a portion of total copper is present in the dissolved form. Stiff (1971) found that 12-57% of the copper in various British rivers was in the dissolved phase, although Perhac (1974) reported 92.3% of the total copper in the dissolved phase in three streams in Tennessee. The particulate forms would include perhaps the oxide, sulfide, and malchite precipitates, in addition to insoluble organic complexes and copper adsorbed onto clays and other solids. Table 26 shows the distribution of copper measurements from STORET for dissolved and total copper in the United States. Though the data are not definitive since they cover all observations for copper in the U.S. over a period of years, and were not necessarily measured concurrently, they indicate that dissolved levels tend to be consistently lower than total levels for copper and suggest that the streams examined by Perhac may be exceptional rather than the norm.

Second, the dissolved portion of the copper may be complexed to various degrees. The equilibria affecting copper in natural waters have been examined by numerous authors (Stiff, 1971; Sylva, 1976; Andrew et al., 1977; Anderson and Morel, 1978; Jackson and Morgan, 1978). Various results have been calculated and measured for different conditions and equilibrium constants, but all models reveal the same general trend. Figure 18 shows calculated copper speciation in a relatively hard fresh water. As shown, in the absence of an organic chelator, the free cupric ion is predominant at low pH; however, its importance drops off rapidly above pH 6.3 and the monocarbonate or the dihydroxide complex become predominant. In the presence of excess NTA, the cupric ion is never significant and organic complexes predominate below pH 8. At higher pH the hydroxide complex is predominant (Elder and Horne, 1978). Though other authors predict that carbonate complexes will be more important (Sylva, 1976), free copper is only clearly significant in acid waters with little potential for organic complexing.

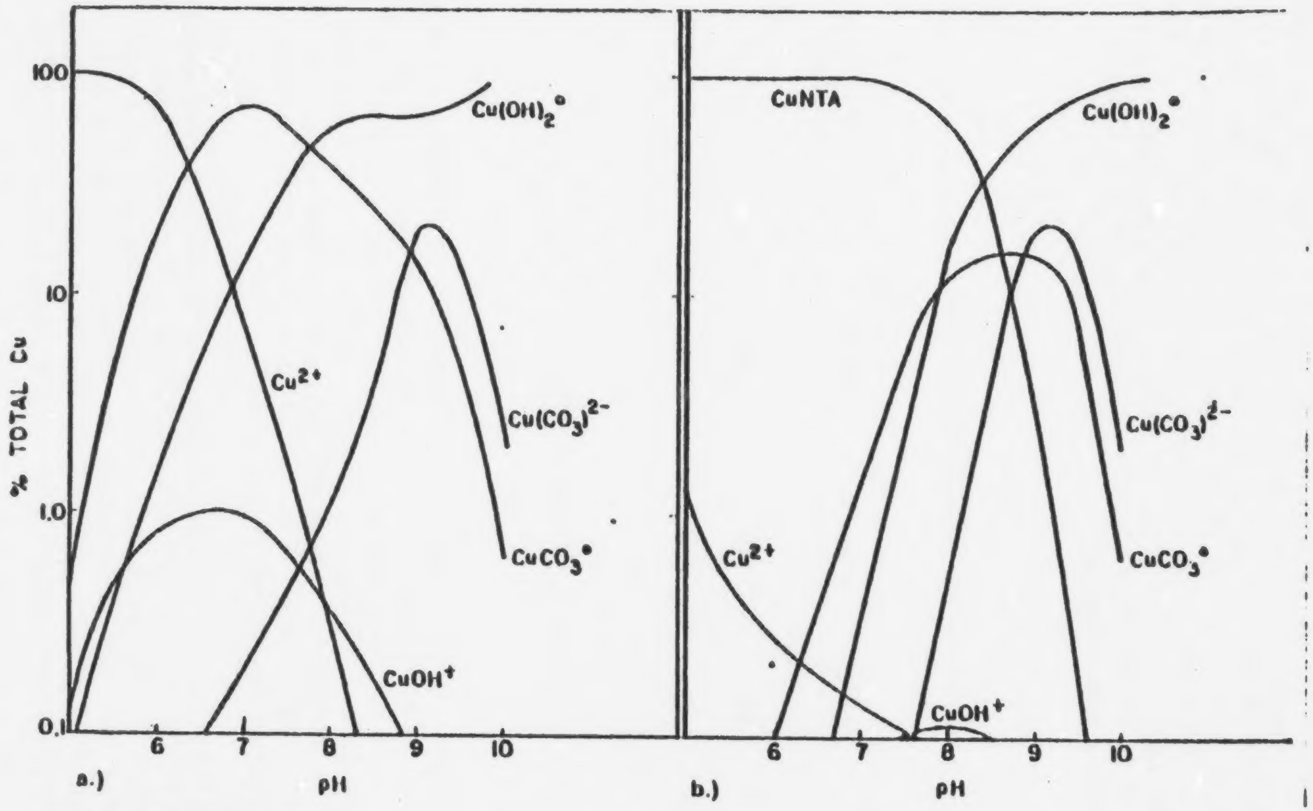
The question remains as to what extent of the copper is complexed by organic material in natural waters. Gächter et al. (1978) looked into

TABLE 26. DISTRIBUTION OF LEVELS OF DISSOLVED AND TOTAL COPPER FROM STORET MONITORING DATA

	Observations in concentration range (%)		
Form of Copper	1-10 μg/L	10-100 μg/L	100-1000 μg/L
Dissolved	63	19	4
Total	41	44	10

Note: this table indicates that most of the measurements of dissolved copper have been in the range of 1-10μg/L. Measurements of total copper are distributed much more heavily in the range of 10-100μg/L.

Source: STORET (1970-1979)



Reference: Elder and Horne (1978).

FIGURE 18. CALCULATED COPPER SPECIATION IN A RELATIVELY HARD FRESH WATER WHERE CONCENTRATIONS OF INORGANIC CARBON = $10^{-2.3}$ M AND CALCIUM = $10^{-2.6}$ M, (a) IN ABSENCE OF ORGANIC CHELATION AND (b) IN PRESENCE OF EXCESS NTA ($[NTA]_{total} >> [Cu]_{total}$)

this question in some detail. They found that copper added to lake water was 65-70% associated with molecules having a molecular weight of greater than 1000. At a total dissolved copper concentration of 5×10^{-8}M (1.45 µg/L), the concentration of free ion is about 5.5×10^{-11}M (1.6×10^{-3} µg/L). Stiff (1971) examined the forms of copper added to various river waters at a concentration of 800 ug/L. In seven locations, the free copper represented 0.1-1.3% of the added copper; carbonate represented 5-54% of the total, and amino acid complexes represented 16-73%. Humic complexes and other unidentified forms of copper were sometimes observed. In two river waters to which no additional copper had been added the following distribution was observed:

	Concentrations (µg/L)				
	Cu^{2+}	$CuCO_3$	Amino Acid Complex	Inert Humic Complex	Hexanol Extractable
River Thames (Lea Marston)	1.8	34	48	n.d.	n.d.
Tributary of R. Churnet	0.5	2	106	n.d.	12

Source: Stiff (1971)

McCrady and Chapman (1979) also investigated the importance of the copper ion in several river waters. All of the samples had a pH of greater than 7.5, low suspended solids, and low total organic carbon. Hardness ranged from 26 mg/L $CaCO_3$ to 132 mg/L $CaCO_3$, with one exception (326 mg/L $CaCO_3$). As expected, the river with the hardest water had the lowest percentage of copper ion (0.45%) as compared with total copper. The rest of the rivers showed a ratio of 1-10%.

The chemical speciation of copper in natural waters has implications for the interpretation of laboratory toxicity data. For some invertebrates, effects appear to be due to the cupric ion. The evidence presented above suggests that the free copper ion in situations where it has been measured is usually less than 2% of the total dissolved copper. In addition, dissolved copper may represent less then 60% of the total copper reported.

In laboratory studies, water is filtered and the concentration of dissolved organic matter is usually low. Thus, the importance of the cupric ion and other possibly toxic inorganic complexes would be much greater than in many natural waters as is shown in Figure 18 and in the work done by Gächter et al. (1978). In addition, it has been shown that some algae secrete copper complexing agents (Swallow et al., 1978; McKnight and Morel, 1979) and thus this capacity would be lost in filtering.

The importance of the copper ion in reconstituted water and well water that might be used in the laboratory was examined by McCrady and Chapman (1979). These authors found that reconstituted soft water contained 9% Cu^{2+} and hard water 1.4% Cu^{2+}. The copper ion comprised 36% of the total copper in well water. This greater importance is due to the lower pH (7.0) and the softness (25mg/L $CaCO_3$) of the well water.

Comparing laboratory data and field data, therefore, requires the consideration of numerous factors, i.e., pH, hardness, the presence of suspended solids, and the availability of organic complexing materials. In a hypothetical example based on the information presented above (Elder and Horne, 1978) a total copper concentration of about 100 mg/L in relatively hard water in the presence of excess chelating agents (compared with copper), at a pH of 7, the cupric ion could represent about 0.2% of the total, and inorganic complexes about 1% of the total (dissolved copper). In the absence of organic chelation, as occurs in the laboratory, and at the same pH, the cupric ion represents about 8%, as does $Cu(OH)_2{}^o$; $Cu(CO_3)^o$ represents about 90%. At a pH of 6, however, the carbonate complex represents about 10%, while the cupric ion represents about 90% of the total dissolved copper. Thus, this explains why hardness is often inversely correlated with the toxic effects of copper in the laboratory. However, it may be that hardness does not affect toxicity in the presence of organic complexing material. In addition, in the presence of organic complexes, copper may be more toxic to some species at a higher pH due to the formation of hydroxy complexes, which may themselves be toxic.

Unfortunately the extent of organic copper complexing is not well documented in the field. It is apparent that without consideration of the chemistry of copper, estimates of risk to biota are unrealistic. Table 19 identifies locations in which copper concentrations are high and water is soft, so that the cupric ion is more predominant. If the loss of effective copper to particulate forms and soluble complexes is not considered, copper appears to present a risk to aquatic organisms in many locations in the U.S. The extent to which these toxic effects are mitigated in particular locations identified by complexation and adsorption is unknown and would have to be studied specifically. In the absence of these more definitive data, however, it can be stated that the greatest risk exists in areas with high total copper, soft water, low concentrations of suspended solids and dissolved organic matter, and with a low pH.

Although regions with high average levels of copper and/or soft water have been identified, the specific sources of copper in these areas have not. The materials balance developed in Section III identified suspended sediment, urban runoff, copper sulfate use, and POTW's as important contributors of copper to the aquatic environment. However, it is difficult to correlate the sources of copper with high ambient copper levels without extensive investigations of specific areas. Numerous industrial operations discharge copper, including electroplating plants, copper wire mills, pulp and paper plants, steam electric power plants, and plants engaged in brass production, and machinery manufacture. In addition, abandoned and active metal mines can be a source of copper to the aquatic environment. These latter sources are most likely to be important in localized areas.

In order to examine further the questions of sources of copper releases and the actual risk to aquatic biota, several situations were examined for which high concentrations of copper have been reported. The goal of this investigation was to determine the representativeness of the STORET data; the types of copper sources; and the availability of fish kill, biological productivity studies, or other studies that could serve to identify the actual impacts on aquatic biota. The areas chosen were the upper Sacramento River, the Coeur D'Alene River, the Gila River, and the Delaware River. The first three locations are areas with active or abandoned copper mines, while the Delaware River is bordered by areas that are heavily populated and highly industrialized. The approach to these investigations and specific results are detailed in the Appendix. Several conclusions can be drawn from this investigation of four case studies. First, the degree to which the data found in the local areas were representative of STORET data appears to be variable. Data generated through state, local, or university studies may or may not be entered on STORET. Less important; but worth noting, is the fact that a significant time lag frequently appears to exist between data availability and its appearance in STORET.

Second, when examined for individual stations, STORET data did appear to represent the general conditions believed to exist in each of the four minor river basins. This reinforces the theory that the high average copper concentrations reported for some major river basins -- or even minor river basins -- are more likely the result of a small number of very high concentrations, than an indication of typical ambient conditions.

The results also point to the importance of the dilution volume and the nature of specific receiving waters in determining the risk potential. For example, in the South Fork of the Coeur D'Alene River, with high heavy metal concentrations due largely to abandoned mines and past mining practices, salmonids are believed to survive spawning runs at periods of high river flow. However, under normal flow conditions, fish failed to survive more than a few hours in river-based cage studies. In Arizona, water is so alkaline that even though streams do not have large dilution volumes, copper and other heavy metals in acid mine drainage entering these streams are precipitated out of solution within short distances of the source.

The above examples point to an additional very important point concerning the representativeness of STORET data: unless STORET data are available for stations in fairly close proximity of each other, it is difficult to define or describe the significance and extent of risk potential. Several additional conclusions can be drawn with respect to risk:

- Portions of several minor basins examined contained copper concentrations that could be considered chronically, if not acutely, toxic to a number of species. Yet, sensitive fish species are known to exist in such locations (for example, in the Sacramento River below Keswick Reservoir; in Coeur D'Alene Lake). Unfortunately, decades of heavy metal releases and habitat modification would make it difficult to assess any alterations in such populations or aquatic communities attributable solely to copper. However, under seasonally variable conditions, fish kills continue to occur in some locations.

- Much historical data is represented by "total" copper measurements. Measurements of dissolved copper are becoming more routine, and studies to address certain aspects of the fate of discharged heavy metals are being done or considered in some of the locations examined here.

- The sources in the Gila, the Coeur D'Alene, and the Sacramento River Basins appear to be primarily abandoned mines and tailings piles, though some active mining is still occurring in some locations. Sources in the Delaware River Basin have not been identified specifically, but include metal plating operations, pipe manufacturers, power plants, steel industries, and POTW's receiving industrial inputs. The relative magnitude of these sources was not determined.

- In all of the case study examples, copper was not the only contaminant of concern, or even the most significant one. Zinc, cadmium and iron are most frequently mentioned as other contaminants of waters affected by mining wastes and drainage; a wider range of organic and inorganic contaminants is present in the Delaware River.

In summary, the case studies verified the importance of understanding the nature and flow volumes of waters being examined, as well as the nature of sources, in understanding the potential significance and extent of risk due to a contaminant. In the case of copper, there seems to be little likelihood that effects can be traced to this contaminant alone. The case studies reinforced the validity of the laboratory findings concerning the role of pH and hardness in modifying copper toxicity. The significance of organic chelation, and specifics of copper fate such as the significance of sediment adsorption or resolubilization potential, were not established in this effort. It is believed that little empirical data are available on these subjects at this time.

In addition to the risks associated with areas such as those described above, it is evident that fish exposed to copper sulfate used as an algicide are at risk. It is likely, however, that this risk is limited to situations in which the algicide is misused or to very specific environmental conditions (e.g., low pH, soft waters, etc.).

B. HUMANS

Except in massive acute doses, copper is virtually nontoxic to man. This results from the following factors, which have been described in the proceding section:

(1) emetic effects limit oral toxicity;

(2) only about 5% of oral dose is absorbed;

(3) humans generally possess good homeostatic mechanisms; and

(4) absorption through the skin is minimal.

Table 27 summarizes levels producing adverse effects in mammals. There is no experimental evidence that copper is tumorigenic, although some indications of mutagenic effects have been reported. Teratogenic effects have primarily been investigated for the purposes of evaluating exposures to copper IUD's. Hamsters have exhibited teratogenic effects and fetal resorption following exposure to high concentrations of copper. However, no evidence exists to suggest that teratogenic effects are associated with the use of IUD's over 10 years of experience with the product.

Table 28 summarizes estimated copper exposure levels for humans. It is apparent that these exposure levels are well below effects level shown in Table 27. Since the effects due to copper appear to be primarily related to acute exposure, these exposures do not appear to represent a risk, since the lowest reported oral lethal dose of copper was 50 mg/kg.

A small subpopulation of humans suffers from a metabolic deficiency involving passive accumulation of copper and sudden releases. This group must reduce copper intake drastically and may be treated with chelating agents to reduce copper availability.

Table 28 also indicates that renal dialysis patients have the potential for exposure to high levels of copper. It should be noted that this exposure is probably overestimated due to the worst-case assumptions made. However, this type of exposure may be of concern since it is intravenous. For comparison, only 5% of ingested copper is absorbed.

TABLE 27. ADVERSE EFFECTS OF COPPER ON MAMMALS

		Lowest Reported Effect Level			
Adverse Effect	Species	Compound	mg/kg Metal	Incidence %	No Apparent Effect Level
Carcinogenesis	Human	Cu-IUD	--	--	50 μg/day for 3 yr
Teratogenesis	Hamster	$CuSO_4$	2.13[1] IV Day 8	6	---
	Hamster	Copper citrate	1.8 IV Day 8	17	< 0.25 mg/kg Cu metal
Fetal Resorption	Hamster	$CuSO_4$	2.13[1] IV Day 8	26	---
	Hamster	Copper citrate	0.25[1] IV Day 8	16	---
Mutagenesis	Escherichia coli	$CuSO_4$	.003 mg/ml[2]	--	.002 mg/ml Cu metal
Emesis	Human	---	10	--	---
Lowest Oral Lethal Dose	Human	$CuSO_4$	50	--	---
Median Oral Lethal Dose	Rat	$CuSO_4$	120	--	---

---

[1] Lowest tested dose.

[2] Survival at this concentration, however, was less than 5%.

Source: See Section VI

TABLE 28. HUMAN EXPOSURE TO COPPER

Route	Exposure mg/day[1]	Exposure mg (metal) /kg (body weight) /day	Population Exposed	Comment
Ingestion Food	1-4	0.01 - 0.06	large (U.S.)	based on analysis of various diets
	7.6	0.11	smaller	based on diet containing liver
Drinking Water	0.3	0.004	large	based on mean concentration of 2595 distribution samples (consumption of 2 L/day)
	17	0.2	very small	based on maximum concentration of 2595 distribution samples
Inhalation	.04	0.0006	very small	based on maximum concentrations near smelters
Dialysis	5	0.07	very small	reported exposure
	240	3.4	very small	exposure calculated assuming tap water concentration of 1 mg/L and 240-L volume for dialysis
IUD	0.5	0.0008	large	measured release rate

[1] For 70-kg body weight with the exception of IUD exposure, for which a 60-kg body weight is assumed.

Source: See Section VI

C. CONCLUSION

This section has described the nature and magnitude of risk of copper exposure for humans and other biota. Aquatic organisms appear potentially to be at risk in numerous locations in the United States, based on monitoring data, toxicity data, and knowledge of the environmental conditions that affect toxicity. Four areas were examined in more detail, and the potential for risk was confirmed as a result of reported fish kills, or reduced species diversity. In many of these areas high copper concentrations appear to be associated with abandoned mines or tailings piles. Although releases from active mines have been largely controlled, the releases from abandoned mines are much more difficult to control. These releases are of particular concern due to the low pH associated with acid mine drainage.

However, the case studies showed that risk was not widespread throughout the minor river basins examined, but limited to very localized situations. Thus the risk to aquatic organisms is probably much more limited than the list of minor river basins implies.

In other cases, the potential for risk appears to be associated with highly industrialized areas, such as the Delaware River. In such a situation, specific contributors to risk cannot be identified without detailed study of the area,since there are many sources such as plating operations, iron and steel manufacture, pipe manufacture, and POTW's.

In addition, the use of copper sulfate as an algicide can represent a risk to aquatic organisms, especially if the material is misapplied. Numerous fish kills have been reported as a result of such incidents.

The information available indicates that copper does not represent a significant risk to humans. Renal dialysis represents the largest potential exposure. The general population is exposed to copper on the order of 0.07 mg/kg/day, and the lowest reported oral lethal dose is 50 mg/kg.

REFERENCES

Anderson, D.M. and F.M.M. Morel. 1978. Copper sensitivity of *Gonyaulax tamarensis*. Limnology and Oceanography 23(2):283-295.

Andrew, R.W., K.E. Biesinger, and G.E. Glass. 1977. Effects of inorganic complexing on the toxicity of copper to *Daphnia magna*. Water Research 11:309-315.

Brown, V.M., T.L. Shaw and D.G. Shurben. 1974. Aspects of water quality and the toxicity of copper to rainbow trout. Water Research 8(10):797-803.

Brungs, W.A., J.R. Geckler, and M. Gast. 1976. Acute and chronic toxicity of copper to the fathead minnow in a surface water of variable quality. Water Research 10:37-43.

Chakoumakos, C., R.C. Russo, and R.V. Thurston. 1979. Toxicity of copper to cutthroat trout (*Salmo clarki*) under different conditions of alkalinity, pH, and hardness. Environ. Sci. Technol. 13(2):213-219.

Elder, J.F. and A.J. Horne. Copper cycles and CuSO algicidal capacity in two California lakes. 1978. Environmental Management 2(1):17-30.

Gächter, R., J.S. Davis, and A. Mares. 1978. Regulation of copper availability to phytoplankton by macromolecules in lake water. Environ. Sci. Technol. 12(13):1416-1421.

Howarth, R.S. and J.B. Sprague. 1978. Copper lethality to rainbow trout in waters of various hardness and pH. Water Research 12:455-462.

Jackson, G.A. and J.J. Morgan. 1978. Trace metal-chelator interactions and phytoplankton growth in seawater media: Theoretical analysis and comparison with reported observations Limnology and Oceanography, 23(2): 268-282.

McCrady, J.K. and G.A. Chapman. Determination of copper complexing capacity of natural river water, well water and artificially reconstituted water. 1979. Water Research 13:143-150.

McKnight, D.M. and F.M.M. Morel. 1979. Release of weak and strong copper-complexing agents by algae. Limnology and Oceanography, 24(5): 823-837.

Perhac, R.M. 1974. Water transport of heavy metals in solution and by different sizes of particulate solids. (NTIS #PB-232 427.)

Shaw, L. and V.M. Brown. 1974. The toxicity of some forms of copper to rainbow trout. Water Research 8:377-382.

Stiff, M.J. 1971. The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. Water Research 5: 585-599.

Swallow, K.C., J.C. Westall, D.M. McKnight, N.M.L. Morel, and F.M.M. Morel. 1978. Potentiometric determination of copper complexation by phytoplankton exudates. Limnol. Oceanogr. 23(3):538-542.

Sylva, R.N. 1976. The environmental chemistry of copper (II) in aquatic systems. Water Research 10:789-792.

U.S. Environmental Protection Agency (U.S. EPA). 1979. STORET.

Van den Berg, C.M.G., P.T.S. Wong, and V.K. Chau. 1979. Measurement of complexing materials excreted from algae and their ability to ameliorate copper toxicity. J. Fish Res. Board Can. 36(8):901-906.

APPENDIX

FOUR CASE STUDIES -- COPPER RISK TO AQUATIC ORGANISMS

I. APPROACH

The purpose of this appendix is to present descriptions of the implications for risk due to copper in four river basins where copper concentrations are high. The inclusion of this appendix was motivated, in part, by the preceding risk assessment. That assessment showed copper levels to be high, on the average, in a number of minor river basins. Assessment of the potential fate of copper illustrated that copper toxicity was likely to be dependent upon a broad range of potential ambient conditions, including pH, calcium carbonate hardness, and the presence of organic complexing agents. Such conditions may be natural or altered by anthropogenic inputs, and are likely to be variable in individual drainages within a minor river basin. Thus, a closer examination of several areas of high copper concentrations was warranted in order to gain a better understanding of risk potential and documented impacts.

The choice of the four rivers to be examined was based on copper levels reported in STORET over the last five years, a desire to include a range of water quality parameters, and a desire to include representations of municipal/industrial activities, as well as mining activities. The final choices of the Upper Sacramento River, the Coeur D'Alene River, the Gila River and associated drainage, and the Delaware River, were admittedly somewhat arbitrary given the number of areas that might have been included. The degree to which these four rivers are representative of risk potential in other drainages with high copper levels would depend on the degree to which they resemble conditions found in other drainages. No attempt was made here to assess such representativeness.

The scope for this appendix was limited to gaining a better understanding of copper fate and risk in four specific environments. The approach was to identify several key federal, state, and in some cases, university personnel who were well acquainted with water quality, sediment and/or biological conditions in each of the four rivers examined. Information was gathered through phone conversations with such individuals on several or all of the following topics:

- The representatives of STORET data:
  - a) in terms of all of the data available;
  - b) in terms of its adequacy to assess the situations that exist.

Preceding page blank

- The types and nature of copper sources.

- The status of compliance and/or special problems.

- Fish kill, biological productivity or other aquatic biological studies that serve to identify risk to copper.

- Knowledge of the fate of copper in the watershed or water body, including resolubilization potential.

In the case of the Upper Sacramento River, additional, readily available data from studies conducted in that drainage were made available to us.* However, in most cases, case descriptions were developed on the basis of the phone conversations held.

II. CONCLUSIONS

This section summarizes some general conclusions that can be drawn from the four special cases described in the section that follows (Section III). While a number of conslusions are neither surprising nor unique to copper contamination, they have important implications for understanding risk based solely on copper measurements.

- In not one case was copper the only contaminant of concern. In fact, in all of the examples cited, the risk potential of other toxicants was at least equally, if not more, significant. In the three western areas where mining activities or abandoned mines represent the major sources, other heavy metals such as Zn, Cd, and Fe, were at least as significant to any toxicity observed.

- There is no question that the dilution volume and the nature of the receiving water has enormous implications for risk. It becomes obvious that the proximity of water samples to sources in combination with dilution volume are important in the actual impacts observed. Source types or the nature of sources are likely to be as important. The result is that risk potential tends to be defined by a number of coincidental parameters which, while generic in nature, tend to be site-specific. Certainly flow volume, pH, the presence of complexing agents rank high among factors.

- The special case studies did reinforce the role of pH and the role of calcium carbonate hardness in copper toxicity. Comparisons among the circumstances and observed adverse effects for the three western examples illustrate this.

---

*Additional data were also sent from Arizona, but proved to be less directly applicable to the drainages being examined.

- Risk due to copper (with other heavy metals) was verified in three of the areas examined. Conversely, examples exist where seemingly high copper levels were not having observable effects.

- Due to the highly variable conditions at each location, generalizations cannot be made concerning the levels at which effects have occurred. Levels of 1-7 mg/L (total copper) in Spring Creek, California result in an area nearly devoid of aquatic life. Levels of 20-100 µg/L below Keswick Dam allow the presence of a local fishery, including salmonids, although fish kills have occurred. In the South Fork of the Coeur D'Alene River, concentrations range from 0.04-1.0 mg/L total copper. Mortality was observed in live box studies, however, salmonids make successful spawning runs through this area.

- Subjects for which site-specific information was obtained are listed below. In a number of cases, these may reflect field research needs.

  -- Significance of organic chelators.

  -- Importance/impacts of sediment adsorption and resolubilization potential.

  -- Risks due to occasional "slugs" discharged.

  -- What happens at salt water/fresh water interface, especially with changes in psecies at that interface.

The following sections give a detailed report of information gathered for each of the case studies.

III. NOTES FROM SPECIAL CASE STUDIES

A. CALIFORNIA: SACRAMENTO RIVER DRAINAGE, VICINITY OF SHASTA LAKE AND KESWICK RESERVOIR

1. Representativeness of STORET Data

The copper data contained in STORET for the Shasta Lake, Keswick Reservoir, Spring Creek Reservoir, and Sacramento River immediately below these reservoirs is reportedly not representative of the amount of data that exists. Because of heavy metal pollution in this portion of the Sacramento River drainage, there is a large amount of water quality data. In specific studies, for example, copper and cadmium measurements have been taken as frequently as twice a day. Much of this information, however, is in the form of internal memo reports. This data, although we have only seen a portion of it, presents a picture of copper contamination essentially similar to the one presented by the STORET data retrieved.

We were made aware of one problem, however, Evidently, dissolved copper measurements in the past have not always been made correctly (it is not clear whether this applies only to state-generated data). Earlier comparisons of total and dissolved metals indicated that a large percentage of copper remained in the dissolved phase even at higher pH's. This prompted a recent (1979/1980) study of the relationship between total and dissolved heavy metals in this drainage. Preliminary results indicate that earlier dissolved metal measurements were, in fact, in error and that dissolved metals are lower than total metal concentrations. Unfortunately, copper analyses were not completed at the time of this writing, and hence, not available.

2. Sources

Abandoned and operating mines, ore dumps, and naturally exposed sulfide minerals are the sources of acid mine discharges in this area with copper historically considered most significant. Acid mine waste from the Spring Creek drainage, which flows into Keswick Reservoir, represents the major source of toxic concentrations of copper and zinc in the upper Sacramento River Basin (Finlayson and Ashuckian, 1979).

Abandoned mines also exist near Shasta Lake. One such example is the acid mine drainage to Squaw Creek, a headwater to Shasta Lake.

3. Circumstances

A number of factors are important for understanding the circumstances surrounding the problems with acid mine drainage in the upper Sacramento River Basin. Metal mining activities began at the end of the 19th century. Thus, problems with acid mine drainage are not new, and preceded the construction of any impoundments on the upper Sacramento River. However, it is generally believed that when Sacramento River streamflow was not controlled, sufficient dilution existed to reduce waste concentrations from acid mine drainage to levels that were evidently tolerated by fish.

The Shasta Dam and Keswick Dam were completed in 1944 and 1950, respectively (see Figure 1). The effect of these dams was to reduce flood flows into the Sacramento River, thereby increasing the proportional contribution of acid mine drainage pollution in Spring Creyk. As a result, numerous fish kills occurred below Keswick Dam in the Sacramento River. To alleviate this problem, the Spring Creek Diversion Dam was constructed in 1963 and releases of water from the resultant reservoir controlled. The release schedules were based on assumptions concerning seasonal dilution volumes available to reduce copper concentrations from Spring Creek. The necessary dilution factors were based on 96-hour static bioassays with juvenile salmonids (Finlayson and Ashuckian, 1979; Finlayson and Wilson, 1979).

It is presently believed that this original release schedule is not providing sufficient protection of resident and anadromous fish in the

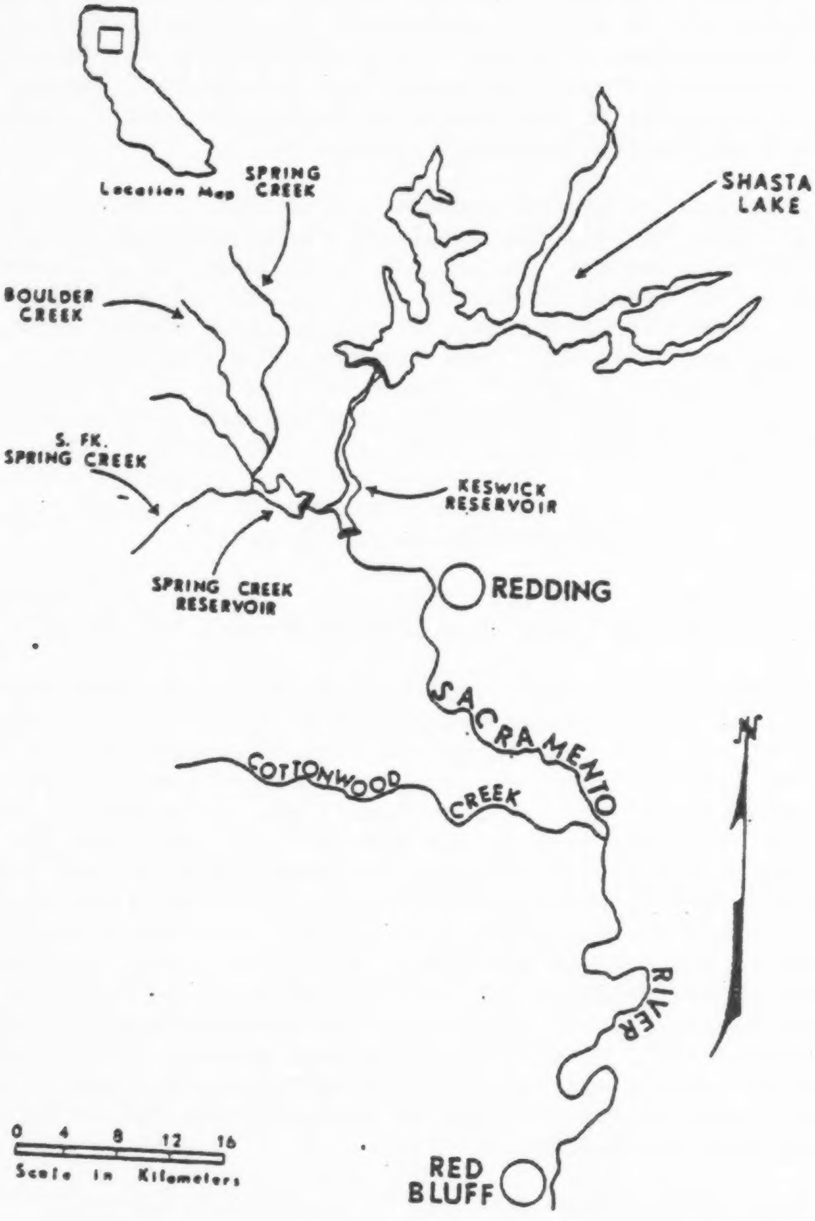

Location Map
SPRING CREEK
SHASTA LAKE
BOULDER CREEK
S. FK. SPRING CREEK
KESWICK RESERVOIR
SPRING CREEK RESERVOIR
REDDING
SACRAMENTO
COTTONWOOD CREEK
RIVER
N
0 4 8 12 16
Scale in Kilometers
RED BLUFF

Figure 1. Location of Spring Creek drainage, Upper Sacramento River basin, California.

SOURCE: Finlayson and Ashuckian, 1979.

Upper Sacramento River, especially considering the existence of life stages more sensitive than juveniles and continuous discharge of waste. Other heavy metals not considered in release schedules, especially zinc, contribute to drainage toxicity, and the contribution of copper has diminished somewhat due to copper cementation plants (for copper removal) located in the Spring Creek drainage. This latter situation has likely resulted in an increase in waste releases from Spring Creek, hence, resultant zinc concentrations are higher in Keswick Reservoir since zinc is not considered in present release calculations.

Water in this portion of the Sacramento drainage is relatively soft (∿40-70 mg/L hardness) so that one would not expect high levels of carbonate complexing with copper. Ambient pH is at least 7 but frequently exceeds a pH of 8. In Spring Creek near the dam, the pH evidently ranges around 3. Over the last couple of years, total copper measurements for the area around Spring Creek Diversion Dam appear to have ranged from slightly below 1 mg/L to over 6 or 7 mg/L. A maximum of 16 mg/L total copper was recorded in 1979, but appears to have been extraordinarily high. Copper concentrations (total copper) below Keswick Dam, in the upper portions of the Sacramento River, appear to range from 0.20 mg/L to around 0.10 mg/L, but more typically in the lower end of the range (STORET; data from California Resources Agency).

From the data reviewed, it is evident that a significant amount of dilution occurs when Spring Creek water enters Keswick Reservoir.

In situ dye studies and bench studies have also been done recently (and are ongoing) to gain a better understanding of the fate of copper and other heavy metals once they enter the Keswick Reservoir. The dye studies indicated that the metal-laden plume entering Keswick Reservoir from Spring Creek hugs the western bank from where it enters, only touching the eastern bank in the area of the Keswick Dam. This pattern of partial mixing is explained, in part, by the description of the Keswick Reservoir as a slow moving river. Studies have also indicated that with initial neutralization of the Spring Creek plume, iron and aluminum are the first metals to come out of solution. In test water of approximately Keswick Dam area pH and hardness (pH 6.5-7.6; 25 to 60 mg/L Ca CO_3), dissolved copper averaged 38.2% of total copper measurements, and dissolved zinc averaged 80.7% total zinc (Finlayson and Ashuckian, 1979). In any case, water quality analyses seem to indicate that significant amounts of these heavy metals are left in the reservoir rather than being discharged into the Sacramento River.

Sediment work has not been done yet in the Keswick Reservoir. A study examining resolubilization potential may be conducted this year. It is not believed that the Keswick Reservoir becomes anoxic during warmer months.

4. Implications for Risk

Because copper inputs into Spring Creek can be controlled, copper concentrations do vary in the creek. Evidently, when copper (metal) concentrations are high, the creek appears to be devoid of life. (Presumably, the pH is also low.) Fish may be found in the creek when concentrations are low. It is here assumed that these would represent recruits from other, non-polluted sources, namely other tributaries to Spring Creek Reservoir.

The west bank of the Keswick Reservoir, where the Spring Creek plume follows the shore, has been described as looking like a desert. This is in contrast to the eastern shoreline, which is lush with vegetation. Fish do exist in the reservoir and are believed to avoid the more heavily contaminated areas.

Fish kills have not been nearly as great a problem in Keswick Reservoir as they have been in the Sacramento River just below Keswick Dam. During the years prior to the construction of the Spring Creek Dam, fish kills were numerous with several being very large (100,000 or more fish). However, a large fish kill occurred below Keswick Dam in 1969, when the ambient pH dropped to about 5.9.

It must be noted that while portions of the Sacramento River, near the dam, have total copper concentrations in the 20-100 μg/L range, the Sacramento River does support a fishery, including salmonids. By one account, the King Salmon population in this area has declined to 30% of what it was 20 years ago. However, the mining drainage situation has not changed for the worse in that time. Rather, the decline is related to the loss of upstream recruitment gravels with dam construction, droughts, and lower dilution volumes due to retaining flood volumes behind the Shasta Dam, especially prior to the Spring Creek Diversion Dam construction.

The result of recent studies in this area has led to the recommendation that discharges from Spring Creek be rescheduled to consider both existing zinc and copper concentrations, and to reduce the Sacramento River dissolved zinc and dissolved copper concentrations below 0.02 and 0.01 mg/L, respectively (Finlayson and Ashuckian, 1979).

Sources of Information

1. Finlayson, B.J. and S.H. Ashuckian. 1979. Safe zinc and copper levels from the Spring Creek drainage for steelhead trout in the Upper Sacramento River, California. Calif. Fish and Game 65(2): 80-99.

2. Finlayson, B. and D. Wilson. 1979. Acid-mine waste: how it affects king salmon in the Upper Sacramento River. Outdoor California 40(6): 8-12.

3. Selected water quality measurements in the Sacramento River near Redding, CA. California Regional Water Quality Control Board - Central Valley Region.

4. Individuals contacted:

- Harry Schueller - California NPDES Program Director (Ca WRCB)
- James Pedri - California Regional Water Quality Control Board, Redding office.
- Brian Finlayson - California Dept. Fish and Game

B. ARIZONA: GILA RIVER DRAINAGE

1. Representativeness of STORET Data

While not a surprising observation, the examination of site specific conditions in this minor river basin pointed to the fact that the data in STORET may not be totally representative of conditions that exist and/or data available in a given area. Three examples from phone conversations concerning the Gila River Basin copper data illustrate that an incomplete picture is being presented, which may introduce biases into an assessment.

a) Evidently, more sampling has been done in locations in which problems have been identified. While it is likely that this situation is not unique to Arizona, it would indicate that the use of this data would bias any conclusions about copper exposure drawn from them. For example, the high copper concentrations and acid conditions reported on the San Pedro River likely represent areas directly impacted by acid mine wastewater or runoff. According to three of the four people contacted, such conditions are localized: the water in this region is so alkaline that acid conditions are quickly neutralized and copper precipitated. The question remains what portion or percent of this drainage area is similarly impacted, and this is a very difficult question to answer based on data that is available.

b) Water quality data for this region that are in STORET at this time represent only a portion of the available data. The Arizona Department of Health has done an assessment of water quality in the Miami-Globe portion of the watershed. This data is not in STORET yet, and the area represents one of the more seriously impacted regions due to copper mining related activities. Data collected by the Arizona Game & Fish Department may not yet be in the STORET system, and a comprehensive study on the Upper Gila completed by a group at the University of Arizona (for the BLM) will likely not be in the system until much later this year.

c) Arizona just recently changed its copper standard from one based on total copper to one based on dissolved copper measurements. Thus the preponderance of historical copper measurements are for total copper (an observation made in the progress of the exposure assessment). In an area where water is alkaline especially, dissolved copper measurements are crucial to an adequate understanding of aquatic exposure. "Total copper" measurements should remain important as they could be used to indicate downstream migration of copper.

While the above discussion applies only to the specific area of Arizona examined, some of the same observations also apply to the area examined in California.

2. Sources

Copper has been mined in this region for nearly 100 years. It is possible that background levels of copper in some areas of outcropping are naturally elevated (>20µg/L), although these cannot be pinpointed at this level of investigation for reasons discussed below.

The copper is mined from open pits and by acid leaching. Significant amounts of sulfide are present in the ore. Thus, acidity and formation of copper sulfate are the consequence. NPDES permits are now required for this process water, which is ponded to allow water to evaporate. There apparently have been examples, recently, of heavy rains (in this generally arid region) causing coffer dams to break or overflow. Thus, this represents one, if a less frequent, source of copper.

In the opinion of both EPA Region 9 and State representatives, a major source of copper is due to earlier mining practices. Abandoned mines (open pit) and tailings piles (which can be 200-300 feet high) are open to oxidation and erosion. One early and apparently frequent practice was to place the tailings piles on the lowest land, often a dry stream bed. (This practice still occurs in Mexico and may explain the extremely high copper numbers observed in the area of that border.) Thus, a major source of copper appears to be due to surface runoff, and hence, not likely to be a problem easily solved. However, specific causes for elevated copper concentrations at particular locations were not pinpointed in this investigation.

3. Circumstances

In better understanding the implications of STORET copper data, it is important to note not only the copper sources but also circumstances in this area of Arizona define its fate.

As noted above, the water in this region is highly alkaline and natural waters contract relatively high levels of phosphates and carbonates. Thus, acid leachate, runoff or pond overflow laden with copper is rapidly neutralized, with copper being precipitated out and becoming associated with either sediments or suspended material. Direct effects on aquatic biota due to copper would appear to be a relatively localized phenomena, with the extent being dependent upon flow volumes. This latter situation was confirmed by agency personnel contacted.

The issue of stream flow volume is especially important as almost all surface water in Arizona is allocated (for irrigation). Thus, major portions of these streams, especially in the drier South, do not have flow at least some of the year (we do not have many samples from STORET in these areas).

In addition, in northern regions, streams have been impounded, with reservoirs representing drinking, irrigation water, and fishery (recreation) resources. Streams flowing into these reservoirs do carry copper (and iron) laden silts. The deeper reservoirs stratify in warmer months with the hypolimnion often becoming anoxic. Under these anerobic conditions, copper, iron, and H_2S are released in a soluble form. Based on the conversations held, it does not appear that extensive investigations concerning the risk potential of reported resolubilization have been conducted.

Most of the fishery in Arizona is a "put and take" salmonid fishery in the more perennial portions of the rivers and the reservoirs. Bass and catfish have also been stocked in the reservoirs, but these are assumed to be reproducing populations.

Review of selected STORET data indicate that, at least for some locations, copper concentrations can be highly variable. For example, at a number of stations along the San Pedro River within the Gila drainage, a wide variation in copper concentrations can be observed. During several months in the late winter/early spring of 1978, the following ranges of "total" copper concentrations were recorded for five different locations:

- 30 to 300 μg/L copper,
- 210 to 6200 μg/L copper,
- 140 to 280 μg/L copper,
- 290 to 730 μg/L copper
- 5 to 2800 μg/L copper.

Similar observations can be made at several additional locations in the Gila drainage. In some cases, $CaCO_3$ hardness and pH are similarly variable. Such observations may be related to differences that are naturally occurring (differences in river flow or leachate due to rainfall) or direct discharges from specific sources that are highly variable.

4. Implications for Risk

There are no fish kill data that we have been able to find. Unfortunately, studies have not been conducted comparing fishery productivity in impacted and non-impacted areas, although this is not surprising considering the nature of the fishery. Tissue analyses are evidently now being done by state personnel on a selected basis.

Below is a list of (verbal) evidence of the observed effects of copper in this region.

a) In flowing streams in the immediate areas impacted by acid copper runoff, etc., streams appear to have no algae or other biota. The situation visibly improves downstream.

b) In some areas such as the one described above, trees in the riparian habitat appear to be adversely effacted by "something," which may be copper. This may be investigated by the Department of Game and Fish this year. The concern over saline irrigation waters dominates water quality considerations, and with the possible exception of citrus production (related to Cu/Boron balance), Cu has not been an issue.

c) There is some evidence that the resolubilized copper, iron, manganese, and H_2S in reservoirs may have impacts on the usability of the recreational fishery. For example, fish from Roosevelt Lake have been brought to state agency personnel with darkened flesh (metallic flavor). Pinal Creek, polluted by mining activities, experienced a fish kill in 1973 or 1974. While copper levels may have been high, the fish kill was attributed to iron, manganese and H_2S.

One study was just completed at Arizona State University on diatom populations in a stream contaminated from a mine seep (data not yet available). It was observed that essentially only one species of diatom inhabited the diatometers in the stream area near the mine seep. A diverse diatom community reappeared on samplers further downstream. Water quality data indicated a mean concentration of 20.9 mg/L dissolved Cu from the mine seep, a mean concentration of 6.47 mg/L dissolved Cu in the creek adjacent to the seep, and a mean concentration of .270 µg/L dissolved Cu 1 km downstream. While data indicate effects of copper, they represent only two 1-month samples, as the creek was dry the rest of the time.

Sources of Information

Region 9 EPA

1) Ted Durst - in charge of NPDES permits for Arizona.

2) Phil Woods (Water Division) - in charge of Arizona.

Arizona Department of Game and Fish

3) Ken Hanks

Arizona Department of Health

4) Timothy Love

Arizona State University

5) Dr. Milton Ray Summerfeld

6) Andrew Lampkin (graduate student)

C. IDAHO: COEUR-D'ALENE-SPOKANE RIVER DRAINAGE

1. Representativeness of STORET Data

Discussions with Idaho Department of Health and Welfare personnel gave a somewhat more encouraging picture concerning the representativeness of STORET data. They believe that much of the general survey data collected on an annual basis is in STORET. Some specialized studies may not be placed in the system.

2. Sources

Mining has been practiced in this area of Idaho for nearly a century. Active mining, smelting, plating, as well as old tailings and abandoned mine drainage represent the major sources of copper observed in surface waters in this system.

While state personnel believe that point source controls have resulted in reduced loading from newer sources, there has evidently not been a marked improvement in ambient concentrations in heavily impacted streams such as the South Fork of the Coeur-D'Alene. Non-point sources of copper and other heavy metals remain a real problem. Two examples illustrate this situation:

a) Houses have been built on old tailings piles in some areas. Even the groundwater may be impacted.

b) In some locations where tailing pond effluents are treated sufficiently, the pond itself leaks, contributing significant amounts of heavy metals to the adjacent river or stream.

3. Circumstances

The fact that water in rivers such as the Coeur-D'Alene are softer and less well buffered than the Gila River is one major difference between the circumstances affecting the significance of ambient levels of copper in waters in Arizona and in Idaho. Other complexing agents (such as organics) that might affect reduced copper toxicity are not believed to be present in high amounts in rivers such as the South Fork of the Coeur-D'Alene. Very low ambient pH has been a real problem in the past, although ambient pH in this river reportedly remains in the 5-7 range now. Ambient pH in other portions of this drainage, the North Fork of the Coeur-D'Alene for example, is typically greater than 7. The water in this area is soft and relatively unbuffered (alkalinity < 20 mg/L; hardness < 50 mg/L).

Small lakes are connected to the Coeur-D'Alene along its course, and the river empties into Coeur-D'Alene Lake which then flows into the Spokane River. According to agency personnel, dissolved oxygen is not a real problem in this drainage. The river has a steep gradient and has been channelized so that the water remains well oxygenated. The lakes are not believed to become anoxic for any period of time. However, Coeur-D'Alene Lake is becoming more eutrophic, thus anoxic conditions could become more of an issue in the future.

While the reported water quality parameters appear to favor the presence of soluble/toxic forms of copper (and other metals) in the water column, studies done in the mid-seventies do show a high level deposition of metals where the Coeur-D'Alene flows into lakes. Concentrations of metals in sediments decreases with distance from the stream mouth. Metal concentrations are also lower in lake water and in the Spokane River. Certainly dilution is likely a major factor in these lower concentrations. The question remains to what degree sediment deposition and increased complexing of metals also play a role. Unfortunately, studies on complexing or the potential for resolubilization from sediments do not appear to exist.

STORET data for this area, from 1978 and 1979, indicate very high copper concentrations at several locations which appear to be discharge (exact type, point or non-point source, etc., was not determined). Even at these locations, total copper concentrations ranged from <40 μg/L to 1 mg/L or more. The data from the South Fork of the Coeur-D'Alene showed copper concentrations within a 10-50 μg/L range. By contrast, data from Coeur-D'Alene Lake Idaho portions of the Spokane River indicated "total" copper concentrations typically <10 μg/L.

While the above discussion focuses on copper fate in this drainage, copper is not considered the major problem. In fact, concern over zinc, cadmium and even iron place copper far down the list of problems considered significant in this drainage. It was acknowledged that while copper could contribute to the problems observed, the concentrations of other heavy metals were so high that it is difficult to isolate copper's role in observed toxicity.

4. Implications for Risk

The effect of high concentrations of heavy metals in the South Fork of the Coeur-D'Alene has been demonstrated. As recently as the Fall 1979, live box studies were conducted in the South Fork, and fish only survived a few hours in the most severely impacted sections of the river. Water quality measurements taken at the time of the in-stream bioassays indicated extremely high levels of Zn (4,000 to 5,000 μg/L), Cd (10 to 25 μg/L), and Fe (perhaps 4,000 to 5,000 g/L). The contact in this case did not recall copper measurements. Data retrieved from STORET indicate several copper measurement maxima in the mg/L range; unfortunately, the summaries do not indicate the time of year these were taken. Interestingly, the cause of fish death in the above-mentioned live-box bioassays was believed to be iron-oxide floc formation on fish gills.

In spite of the above obvious toxicity of the South Fork, it has been shown recently that fish (importantly, salmonids) do make successful spawning runs through this stretch of river to the unpolluted North

Fork. Successful upstream migration is believed to occur during high flows, when heavy metals inputs are diluted.

While the STORET data on copper collected for Coeur-D'Alene Lake and the Upper Spokane River indicate a general reduction in ambient copper concentration, ambient levels of heavy metals in a large number of cases evidently exceed recommended maxima for water as "soft" as is present here. Nonetheless, a significant fish population, including salmonids, exists in this portion of the drainage. Studies done in the mid-seventies indicated significant elevations in heavy metals in the tissues of algae and periphyton, aquatic macrophtes and fish, and on trees adjacent to the Spokane River. To our knowledge, studies of the effects of such concentrations of heavy metals, such as decreased productivity, have not been done. Obviously, the acutely toxic effects of the heavy metals do not exist.

A better understanding of the fate of copper and other heavy metals in this drainage might be extremely helpful. Certainly, dilution plays a role in terms of both seasonal and downstream reduced toxicity. Reported high concentrations of heavy metals in lake sediments (both Coeur-D'Alene Lake and lakes adjacent to the South Fork) indicate (not surprisingly) that precipitation, sediment and/or suspended solids adsorption of metals do play a role in removing heavy metals even though ambient conditions do appear to favor soluble forms of the metals. Unfortunately, the degree to which organics, colloids, as well as inorganic substances in the water column may be acting to reduce heavy metal toxicity is unknown. Similarly, the potential from sediments has not been investigated.

Sources of Information

Region 10, EPA

Ron Kreitzenback (Water Quality)

Ray Peterson (Biota)

Idaho, Department of Health and Welfare

Lany Koenig (Industry Source Control)

Mike Smith (Special Water Studies)

D. THE DELAWARE RIVER BASIN

1. Representativeness of STORET Data

The Delaware River/Estuary flows through or touches on five different states. Hence, there are a large number of city, state and/or federal agencies that collect data or support data collection efforts. The Delaware River Basin Commission represents an interstate group that also supports data collection.

Based on discussions with a representative sample of these various authorities, it does appear that much of the water quality data collected is entered in STORET, although at least in the case of the larger data collection programs there may be as much as a year's lag time between collection and STORET entry.

In some cases, however, the data may be somewhat misleading due to a variety of analysis techniques with various detection limits. Where "Standard Methods" have been used, the detection limit is 10 µg/L; the STORET data indicate that some analytical methods used have a detection limit below 10 µg/L; and analytical methods used for copper measurements for the Basin Commission have a 100 µg/L detection limit. Some of the samples analyzed for the New Jersey Department of Environmental Protection may represent data of dubious quality because a laboratory did not follow required procedures concerning holding times.

2. Sources

The Delaware River Basin contains areas of heavy population concentrations and industrial development. While no attempt was made here to catalog sources and connect them directly to areas of higher copper concentration, the types of sources are numerous. While concentrated in more industrialized sections of the drainage, some sources are also found in less developed areas. The types of sources include metal plating industries, pipe manufacturing, effluents from power plants using certain corrosion inhibitors, steel industries, and even from copper pipes used in water systems. The latter source, while not likely producing high concentrations of copper, can serve as a copper source due to the slightly acid nature of the water. Industrial sources may discharge independently or they may send effluents to a POTW. In the City of Philadelphia, these two different routes are about equally represented.

3. Circumstances

The Delaware River/Estuary, as this designation implies, is a fairly large freshwater river, becoming an increasingly saline-well mixed estuary in its southern reaches.

Looking at STORET data from the Delaware Drainage, there are a number of samples where copper levels are reported at 100 µg/L. Assuming that these all represent copper measured by a technique with a 100 µg/L detection limit, copper levels in most of this drainage are 10 µg/L or less. The exceptions appear to be in the heavily industrialized areas (Trenton-Philadelphia corridor) and upstream near Martins Creek. With few exceptions, total copper levels in this area fall in the <10 to 80 µg/L range (one measurement near Martins Creek was 170 µg/L Cu).

Very little sediment work has been done. None of the persons contacted had an idea of what may be complexing heavy metals in this drainage, as water is both fairly soft and somewhat acid.

4. Implications for Risk

No information on fish kills or other effects was uncovered. A benthos survey has been done that indicates changes in diversity and number in various portions of the river. It does not appear that this had been tied directly to a particular contaminant, although this would likely be impossible. From the discussions held, it is fair to conclude that risk due to copper is of minor concern compared with other contaminants potentially and known to be present.

Sources of Information

Delaware River Basin Commission - Cy Gross

City of Philadelphia - Dennis Blair

New Jersey Department of Environmental Protection

Nick Binder - Basin Manager
Frank Takacs - Biologist
Robert Kotch - Water Quality/Data Collection

Paul Hamer - NJDEP, Bureau of Fisheries
Robert Ahlert - Bureau of Engineering Services at Rutgers University